Spectroscopic studies of Er\(^{3+}\) doped Ge-Ga-S glass containing silver nanoparticles

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**Abstract**

The spectroscopic characteristics of an erbium-doped Ga\(_9\)Ge\(_{25}\)Ga\(_{10}\)S\(_{65}\) (GGS) glass containing silver were studied and compared with that of an erbium-doped GGS glass without silver. The optical absorption spectra revealed the surface plasmon resonance (SPR) related characteristic of silver nanoparticles (NPs) around 490 nm. Enhancement of Er\(^{3+}\) luminescence was observed for a broad excitation wavelength region, and the largest enhancement was observed for the excitation at 488 nm, which is near the peak of SPR of silver NPs in GGS glass and in resonance with Er\(^{3+}\) ions. For the excitation at 405 nm, enhancement of luminescence from both GGS host and Er\(^{3+}\) ions was observed. A smaller enhancement was observed for a two-step upconversion luminescence excited at 801 nm. The observed enhancement of Er\(^{3+}\) luminescence is mainly attributed to the local field effects: the SPR of Ag NPs causes an intensified electromagnetic field around NPs, resulting in enhanced optical transitions of Er\(^{3+}\) ions in the vicinity.

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1. Introduction

Rare-earth doped chalcogenide glass Ge-Ga-S system is promising for applications in optical devices such as optical fiber amplifiers, lasers, and optical converters of infrared radiation to visible regions, etc. [1–8]. In addition to the common advantages of low-phonon energy, good infrared transparency, good chemical durability, large refractive index, and good glass-forming ability of some other chalcogenide glasses, the Ge-Ga-S system has a relatively larger band gap among chalcogenide glasses and a better rare-earth doping ability than that of the Ge-Sb-S system [9,10].

The incorporation of metallic nanoparticles (NPs) in rare-earth doped glasses may enhance the luminescence of rare-earth ions when the excitation or emission is near the surface plasmon resonance (SPR) wavelength of metallic NPs [11,12]. The metallic NPs in the vicinity of rare-earth ions may enhance the rate of excitation and emission of rare-earth ions. This effect is attributed to local field enhancement on excitation and emission of rare-earth ions or energy transfer due to an intense local electric field induced by SPR [11–13]. Coupling rare-earth ions with metallic NPs has been developed as a valuable strategy to improve the luminescence yield of rare-earth ions [13–18]. The rare-earth doped glasses containing metallic NPs are therefore attracting great interest, and most have been reported in rare-earth doped oxide glasses [13–18], while few have been reported on chalcogenide glass [2]. V. K. Rai et al. recently reported the enhancement of frequency upconversion at 494 nm of Pr\(^{3+}\) in Ge-Ga-S glass containing silver NPs, excited by pulsed laser at ∼590 nm [2].

In present work we report visible and infrared to visible upconversion luminescence of Er-doped Ge-Ga-S glass containing silver NPs, compared to that of a glass without silver co-doping. The excitation wavelengths used were at 405 nm, 488 nm, and 801 nm. The light at 405 nm is strongly absorbed by the host Ge-Ga-S glass and can excite Er\(^{3+}\) to the \(^4\)I\(_{15/2}\) level; the light at 488 nm is near the center of the SPR of silver NPs, and in resonance with the transition \(^{4}\)I\(_{15/2}\) → \(^{4}\)F\(_{7/2}\) of Er\(^{3+}\) ions; and the infrared light at 801 nm first excites Er\(^{3+}\) to the \(^{4}\)I\(_{15/2}\) level and successively to the \(^{4}\)F\(_{1/2}\) level [19–21]. Other characterizations conducted include Raman scattering, optical absorption, and lifetime of transitions \(^{4}\)S\(_{3/2}\) → \(^{4}\)I\(_{15/2}\) and \(^{4}\)F\(_{9/2}\) → \(^{4}\)I\(_{15/2}\) of Er\(^{3+}\) ions in GGS glass.

2. Experiment

High-purity elements Ge, Ga, S, Er, and Ag\(_2\)S (5N or 4N purity) were used as raw materials. The compositions of three batches are: Ge\(_{25}\)Ga\(_{10}\)S\(_{65}\) (GGS), GGS + Er\(_{6}\)O\(_{3}\), and GGS + Er\(_{6}\)O\(_{3}\)(Ag\(_2\)S)\(_{0.5}\), where the subscript number represents the mol\% of each composition. The mixtures were sealed into a silica ampoule (OD/ID = 16/10 mm) under a vacuum of better than 5 × 10\(^{-5}\) torr. The sealed ampoule was then put into a tubular furnace and heated up to 920 °C at 1.0 °C/min, and homogenized for 10 h at 920 °C through a continuous horizontal rotation to allow thorough reaction of the compounds [22]. The rotation was then stopped and the tube furnace with ampoule was rotated to a vertical position. The temperature was then reduced down to 800 °C for 20 min to reduce the formation of bubbles. The ampoule was then put out from the furnace and quenched into water at room temperature. The glass was then annealed at 370 °C for 10 h and slowly cooled down to room temperature to release the stress and to nucleate silver NPs. Finally, a yellowish glass rod was obtained by cutting the silica ampoule. The glass of all three batches appears to be...
of good optical quality. Polished samples of 1.5 mm in thickness were used for optical measurements.

The Raman spectrum was taken using a right-angle scattering geometry on a double-grating spectrometer (Spex Model 1403) with a thermo-electric (TE) cooled photomultiplier (PMT) (Hamamatsu R943-02) and a photon-counting system. The excitation source used was an argon ion laser operating at 514.5 nm. The upconversion luminescence was taken using the same system with an excitation source at 801 nm from a cw Ti:sapphire laser. The incident laser power was 35 mW and the estimated intensity at focus is about $3.0 \times 10^4$ W/cm$^2$. The luminescence emission and excitation spectra were taken using HORIBA FL3-11 Spectrofluorometer with a xenon lamp, and the lifetime measurements were taken using HORIBA FluoHub-B with a pulsed SpectraLED, operating in the multichannel scaling (MCS) mode.

3. Results

3.1. Raman spectra

Fig. 1 shows the Stokes Raman spectra of GGS glasses with and without Ag co-doping, from 0 to 600 cm$^{-1}$, excited at 514.5 nm. The Raman spectrum of GGS glass doped with 0.5 Ag$_2$S is almost the same compared to that of the undoped GGS glass because of the low concentration of Ag. The strongest band at 342 cm$^{-1}$ is due to the symmetrical stretching vibration of $[\text{GeS}_4]$ and $[\text{GaS}_4]$, while that at about 112 cm$^{-1}$ is associated with asymmetrical bending vibration of $[\text{GeS}_4]$ and $[\text{GaS}_4]$ [5,10,23]. The band at about 428 cm$^{-1}$ originates from the vibration of $\text{S}_3\text{Ge-S-GeS}_4$, and the band at about 268 cm$^{-1}$ originates from vibration of $\text{S}_3\text{Ge(Ga)-Ge(Ga)}\text{S}_3$ [5,10,23]. This Raman spectrum is consistent with previously reported results, indicating that the basic structural units in our GGS glass are $\text{GeS}_4$ and $\text{GaS}_4$ tetrahedra which are connected through bridging sulfur to form a three-dimensional network structure [5,10,23]. According to previous reports, the doped rare-earth ions may cause the formation of non-bridging sulfurs and play a charge-compensating role for these non-bridging sulfurs [5,24,25]; and the Ag ions may be reduced and nucleated to metallic NPs after the heat-treatment [2]. Raman spectrum indicates that the highest-energy phonon band in GGS glass is at 428 cm$^{-1}$, which is much smaller than that of common oxide glasses (800–1200 cm$^{-1}$), and also smaller than that of heavy-metal fluoride glasses (~500 cm$^{-1}$). A much smaller multiphonon decay rate of rare-earth ions in GGS glass is therefore expected [19,26].

3.2. Optical absorption and luminescence

Er-doped GGS sample and Er and Ag co-doped GGS sample were measured under the same experimental conditions for comparison. Fig. 2 shows the visible and near-infrared transmittance spectra from 400 nm to 1600 nm measured for Er-doped GGS glass (curve a) and Er and Ag co-doped GGS glass (curve b). The absorption bands associated with Er$^{3+}$ ions were observed in both samples. Significant difference between two samples was observed near the absorption edge. Curve (c) represents the optical transmittance difference between curve (a) and curve (b), indicating the absorption due to Ag co-doping. In addition to the absorption peaks of Er$^{3+}$, curve (c) displays a broad absorption band maximum at around 490 nm which is characteristic of SPR of Ag NPs [11,13]. The GGS sample with Ag co-doping is expected to have silver NPs in the GGS glass matrix because of the thermal annealing during the glass fabrication [2]. The exact
size of the silver NPs is unknown, but can be estimated using the relation [27,28]

\[ R = \frac{V_f}{\Delta \omega} \]

where \( R \) is the average crystal radius, \( V_f \) is the Fermi velocity of an electron and is \( 1.39 \times 10^6 \text{ m/s for Ag} \), and \( \Delta \omega \) is the full width at half maximum of the Plasmon absorption in angular frequency. The estimated value of average radius is 2.9 nm. This estimated value falls within the range of 1.5 to 3.5 nm reported by V. K. Rai et al. for a GGSAgPr glass [2]. The SPR wavelength of spherical NPs calculated using Mie theory in GGS glass matrix is about 485 nm [2,29,30]. The observed absorption band peaked around 490 nm therefore provided a reasonable agreement with SPR of silver NPs.

The luminescence spectra were measured for samples with and without silver NPs, using 488 nm and 405 nm excitation, respectively. The top part of Fig. 3 shows luminescence spectra excited at 488 nm. For light at 488 nm excitation, strong visible luminescence of the emission \( ^4S_{3/2} \rightarrow ^4I_{15/2} \) centered at 550 nm and emission \( ^4F_{9/2} \rightarrow ^4I_{15/2} \) centered at 665 nm was observed. The luminescence intensity from the sample with silver NPs is about twice the intensity of the sample without silver NPs. The bottom part of Fig. 3 shows luminescence spectra excited at 405 nm. The light at 405 nm is strongly absorbed by the GGS host, and it may also excite Er\(^{3+}\) ions to \(^2H_{9/2}\) level [21,26]. Luminescence from both GGS host and Er\(^{3+}\) ions was observed. Two luminescence bands from Er\(^{3+}\) ions are superposed on the host luminescence. The luminescence from GGS host is gradually reduced in intensity from 500 nm to 650 nm. The luminescence from GGS host and Er\(^{3+}\) ions (\(^4S_{3/2} \rightarrow ^4I_{15/2}\)) is simultaneously enhanced from the sample containing silver NPs compared to that without silver NPs. The enhancement is stronger at shorter wavelength which is closer to SPR of silver NPs.

Fig. 4 shows the excitation spectra for luminescence at 665 nm as the excitation wavelength tuning from 400 to 640 nm. The excitation spectra provide evidence for the enhanced excitation of Er\(^{3+}\) ions due to SPR of silver NPs, and the enhancement depends on the wavelength. Significant enhancement of luminescence was observed for excitation wavelength between 480 and 560 nm. The largest enhancement is near 488 nm, which is about the peak wavelength of SPR of silver NPs and in resonance with Er\(^{3+}\) ions in glass [21,26].

With pulsed LED excitation, luminescence decay curves at 550 nm and 665 nm were recorded. Fig. 5 shows the luminescence decay curves for sample with and without silver NPs. The luminescence decay curves are almost exponential in all cases. For transition \(^4S_{3/2} \rightarrow ^4I_{15/2}\), the measured lifetime is \( 88 \pm 3 \) \( \mu \)s and \( 97 \pm 3 \) \( \mu \)s for the samples with and without silver NPs. For transition \(^4F_{9/2} \rightarrow ^4I_{15/2}\), the measured lifetime is \( 135 \pm 5 \) \( \mu \)s and \( 171 \pm 5 \) \( \mu \)s for the samples with and without silver NPs. The emission lifetime has a small decrease for sample with silver NPs.
3.3. Upconversion luminescence

Fig. 6 shows upconversion luminescence from Er-doped GGS glasses with and without silver NPs, excited by infrared laser at 801 nm. This upconversion luminescence involves two-step successive excitations by 801 nm laser: the first step is \( ^4I_{15/2} \rightarrow ^4I_{11/2} \) and the second is \( ^4I_{11/2} \rightarrow ^4F_{3/2} \), where \( ^4I_{11/2} \) level is populated by multiphonon relaxation from \( ^4I_{9/2} \rightarrow ^4I_{11/2} \). [20,21,31]. The strongest emission band centered at 550 nm is corresponding to the transition \( ^4S_{3/2} \rightarrow ^4I_{15/2} \), whereas other two weaker bands are transition \( ^2H_{11/2} \rightarrow ^4I_{15/2} \) centered at 528 nm and transition \( ^4F_{5/2} \rightarrow ^4I_{15/2} \) centered at 665 nm [20,21,31]. The enhancement of upconversion luminescence was observed as shown in Fig. 6, where the emission \( ^4S_{3/2} \rightarrow ^4I_{15/2} \) is about 35 % stronger for the sample containing silver NPs.

4. Discussion

The enhancement of rare earth luminescence influenced by SPR of metallic NPs is generally attributed to two mechanisms: the local field enhancement (LFE) and the energy transfer between rare-earth ions and metallic particles [11–17]. The effects of energy transfer between ions and particles are twofold: they may enhance luminescence by energy transfer from particles to ions and may quench luminescence by energy transfer from ions to particles [10–13,32]. Luminescence quenching occurs at high particle volume fraction or large particle size [11–13], which may not be significant in our case (~2.9 nm). SPR excitation results in giant and highly localized electric field around the Ag NPs, which may greatly enhance the transition yield of rare-earth ions in the vicinity of Ag NPs [11,13,28]. The interaction between Er\(^{3+}\) and Ag NPs strongly influence Er\(^{3+}\) ions owing to their electronic plasmon resonances, causing an intensified electromagnetic field around Er\(^{3+}\) ions, resulting in an enhancement of luminescence from Er\(^{3+}\) ions [11–14]. According to O. L. Malta’s discussion on the luminescence of the Eu\(^{3+}\) ion in the presence of small metallic particles, the enhancement factor is peaked around \( \omega = \omega_{0}n_{0} \), where \( \omega \) is the absorption/excitation frequency and \( \omega_{0} \) is the SPR frequency of the metallic NPs [11]. The host matrix, binding state, size and shape of metallic NPs, and distance between the rare-earth ion and NPs are also important in LFE and discussed previously [11–13]. According to local field effects, there is an additional interaction between electromagnetic field and rare-earth ions due to the very high field gradients near a metallic particle [11,12]. The expressions for Lorentz local-field correction for the various mechanisms of absorption and emission of light are \( F_{\text{abs}}/E_{0}^{-n} \) for absorption and induced emission and \( E_{\text{em}}/E_{0}^{-n} \) for spontaneous emission, where \( E_{0}, E_{\text{abs}}, \) and \( n \) are the incident field, the local effective field in the medium and the index of refraction of the medium, respectively [11,33]. GGS glass matrix provides an excellent and convenient host for Er doping and for producing silver NPs. The excitation of SPR of silver NPs in the vicinity of Er\(^{3+}\) ions leads to the observed enhancement of Er\(^{3+}\) luminescence. Fig. 7 shows the scheme of energy levels for GGS host, SPR of silver NPs, and Er\(^{3+}\) ions and the possible transitions and interaction. We observed the largest luminescence enhancement for 488 nm excitation shown in Fig. 3 (top), the light at 488 nm is near the center of the SPR and in resonance with \( ^4I_{9/2} \) level of Er\(^{3+}\) ions. According to LFE mechanism, the excitation of \( ^4I_{15/2} \rightarrow ^4F_{7/2} \) can be significantly enhanced due to SPR of silver NPs. The successive \( ^4S_{3/2} \) and \( ^4F_{9/2} \) levels are populated via multiphonon relaxation [19,26]. The significantly increased population at \( ^4S_{3/2} \) and \( ^4F_{9/2} \) levels provides a significantly increased intensity for emission at 550 nm and 665 nm. The emission rate at 550 and 665 nm may also be enhanced by LFE due to SPR excitation. For excitation at 405 nm, the incident light is mostly absorbed by GGS host because the absorption cross-section of the GGS host is much larger than that of Er\(^{3+}\) ions at this wavelength. The enhancement of luminescence from both GGS host and Er\(^{3+}\) ions can be attributed to the LFE. The luminescence intensity of Er\(^{3+}\) ions is lower using 405 nm excitation compared to that using 488 nm excitation because most of the GGS absorbed energy is dissipated inside the glass matrix for 405 nm excitation. The excitation spectra in Fig. 4 demonstrated the SPR enhanced excitation and its wavelength dependence for emission at 665 nm. The significant enhancement is at excitation wavelength near SPR of silver NPs, consistent with the theory of the LFE due to SPR of silver NPs [11]. The upconversion luminescence was excited at 801 nm; where the first step excitation \( ^4I_{15/2} \rightarrow ^4I_{9/2} \) is far away from SPR, and not likely to have a significant local field enhancement in this case. However, the second step excitation \( ^4I_{11/2} \rightarrow ^4F_{7/2} \) reaches an energy level near the center of SPR of silver NPs as shown in Fig. 7. This second step excitation is possibly accomplished by SPR excitation. Both excitation and emission can be enhanced due to the LFE of silver NPs, which may account for the observed 35% increase in luminescence intensity.

5. Conclusion

We have presented the spectroscopic characteristics of an erbium-doped Ga\(_{10}\)Ge\(_{25}\)S\(_{65}\) (GGS) glass containing silver and compared to that of an erbium-doped GGS glass without silver. GGS glass matrix
provides an excellent and convenient host for Er doping and for producing silver NPs. The SPR related characteristic of silver NPs around 490 nm has been observed in optical absorption spectra. Significant enhancement of Er\(^{3+}\) luminescence was observed. The largest enhancement was observed for the excitation wavelength at 488 nm, which is near the peak of SPR of silver NPs in GGS glass and in resonance with Er\(^{3+}\) ions. The observed enhancement of Er\(^{3+}\) emission is mainly attributed to the LFE on the excitation and emission of Er\(^{3+}\) ions provided by the SPR excitation. Our results suggest that the rare-earth doped chalcogenide glass GGS containing metallic NPs may have potential to have enhanced luminescence for device applications.

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