Plasmon enhanced luminescence of Tb$^{3+}$ doped Li$_2$O-LaF$_3$-Al$_2$O$_3$-SiO$_2$ glass containing Ag nanoparticles

Department of Physics, Fisk University, Nashville, TN, USA 37208

ABSTRACT

Tb$^{3+}$ and Ag co-doped glass nano-composites are synthesized in a glass matrix Li$_2$O-LaF$_3$-Al$_2$O$_3$-SiO$_2$ (LLAS) by a melt-quench technique. The nucleation and growth of Ag nanoparticles (NPs) were controlled by a thermal annealing process. A broad absorption band peaking at about 420 nm was observed due to surface plasmon resonance (SPR) of Ag NPs. Annealing of glass samples results in the growth of Ag NPs. Photoluminescence (PL) emission and excitation spectra were measured from glass samples with different Ag concentrations and different annealing times. Plasmon enhanced Tb$^{3+}$ luminescence was observed at certain excitation wavelength regions. Luminescence quenching was observed for samples with high Ag concentration and longer annealing time. Our luminescence results suggest that there are two competitive effects, enhancement and quenching, acting on Tb$^{3+}$ luminescence in the presence of Ag NPs. The enhancement of Tb$^{3+}$ luminescence is mainly attributed to local field effects: the SPR of Ag NPs causes an intensified electromagnetic field around the NPs, resulting in enhanced optical transitions of Tb$^{3+}$ ions in the vicinity. The quenching effect in the presence of Ag NPs suggests an energy transfer from Tb$^{3+}$ ions to Ag NPs. The competition between the plasmonic enhancement and the quenching effect is discussed for samples with different Ag concentrations and annealing times.

Keywords: Ag, nanoparticle, SPR, Tb$^{3+}$, luminescence

1. INTRODUCTION

Rare-earth doped glasses are important for applications in optical devices such as scintillators, optical fiber amplifiers, lasers, optical converters of infrared radiation to visible regions, etc. In addition to the common advantages of low-cost, large-volume production possibility and easy shaping of elements of glasses, oxide glasses generally possess good mechanical strength, chemical durability, and thermal stability. Tb-doped Li$_2$O-LaF$_3$-Al$_2$O$_3$-SiO$_2$ (LLAS) glass was previously reported to have good photoluminescence (PL) and β-induced luminescence light-yield for scintillator application.

The incorporation of metallic nanoparticles (NPs) in rare-earth doped glasses may enhance or quench the luminescence of rare-earth ions. The enhancement has been attributed to local field enhancement effects on excitation and emission of rare-earth ions and energy transfer from metallic NPs to rare earth ions due to the excitation of SPR of metallic NPs. The quenching effect is due to energy transfer from ions to the metallic NPs. Rare-earth doped glasses containing metallic NPs have recently attracted great interest. However, in spite of the large amount of work published on this topic, the mechanism of energy transfer from metallic NPs to rare earth ions has not been clarified.

In order to further understand the interaction between metallic NPs and rare earth ions in glass, we have studied Tb-doped LLAS glass containing Ag NPs. In present work, we report optical absorption, photoluminescence emission and excitation of Ag co-doped LLAS:Tb glass with different Ag concentrations and annealing times, and discuss the possible mechanisms for plasmonic enhancement and quenching effects on Tb$^{3+}$ luminescence.

2. EXPERIMENT

Reagent grade anhydrous oxide powders of Li$_2$CO$_3$, LaF$_3$, Al$_2$O$_3$, SiO$_2$, TbF$_3$, and AgNO$_3$ were used to prepare glasses. The compositions of lithium-lanthanum-aluminosilicate glass were 28Li$_2$O-11LaF$_2$-6Al$_2$O$_3$-55SiO$_2$ (LLAS). Four

* zpan@fisk.edu
samples containing the same TbF₃ concentration of 1.0 mol % and four different AgNO₃ concentrations of 0.0 mol %, 0.1 mol %, 0.2 mol %, and 0.5 mol %, were prepared. Batches of 30 grams were thoroughly mixed in an agate mortar, and further mixed in a Ball Mill for four hours. The mixture was melted in a platinum crucible at a temperature of 1430 °C. The melts were held for 50 minutes and then cast onto a copper plate and pressed by another copper plate from the top, forming a glass disk of about 4 mm in thickness. The glasses were subsequently annealed at 330 ºC for 15 minutes and then allowed to cool to room temperature in the furnace. Clear glasses were formed for all batches with different Ag concentrations. These glasses appear to be of very good optical quality, with no visual evidence of devitrification. Further thermal annealing was performed at 480 ºC in air. UV-visible absorption was measured from 300 to 600 nm using a Cary dual beam spectrophotometer. PL was measured using 325 nm laser excitation. The excitation spectra were taken using HORIBA FL3-11 Spectrofluorometer with a xenon lamp.

3. RESULTS

3.1 Optical absorption due to SPR of Ag NPs in LLAS:Tb glass

![Absorption Spectra of Ag in LLAS:Tb Glass](image)

*Figure 1. Optical absorption spectra of Ag co-doped LLAS:Tb glass: (a) 0.1 mol % Ag, (b) 0.2 mol % Ag, and (c) 0.5 mol % Ag. Annealing is at 480 °C in air. The SPR absorption band centered at 420 nm grows up with increasing annealing time.*
Figure 2. Peak absorbance due to SPR of Ag NPs versus annealing time: (a) 0.1 mol % Ag, (b) 0.2 mol % Ag, and (c) 0.5 mol % Ag. The data are fitted with second-order polynomials.

Fig. 1 shows the optical absorption spectra of three samples doped with 0.1 mol %, 0.2 mol %, and 0.5 mol % Ag. The spectra were taken for increasing annealing time intervals in hours (h). The annealing was performed at 480 ºC in air atmosphere. Absorption peaks from Tb3+ ions were difficult to observe because of the weak intra-4f transition in nature. A strong and broad absorption band (spreading from 320 to 520 nm) peaked at 420 nm was dominantly observed. This absorption band is the characteristic of SPR of Ag NPs in glass 7,8,10. The amplitude of this absorption band increases for increasing annealing time. The increase of absorbance is significantly faster for sample with a higher Ag concentration. The peak absorbance reaches 4.0 in 48 h annealing for sample with 0.1 mol % Ag and in less than 4 h for sample with 0.5 mol % Ag. It is generally believed that thermal annealing causes reduction of Ag ions and growth of Ag NPs, resulting in increase of the Ag NPs concentration and size in the glass matrix 7,8. The observed increase of absorbance due to SPR of Ag NPs is therefore expected. The exact size of the Ag NPs is unknown, but is estimated in the region of 2 – 16 nm 7,8.

Fig. 2 shows the peak absorbance as a function of annealing time for three samples doped with 0.1 mol %, 0.2 mol %, and 0.5 mol % Ag. The data are well fitted with second-order polynomials. The slope of the curve represents the rate of absorbance increase with annealing time. The rate is largest for the sample with 0.5 mol % Ag and smallest for the sample with 0.1 mol % Ag, which suggests that the growth of Ag NPs is faster for samples with a high Ag concentration.

3.2 Plasmon enhanced Tb3+ luminescence excited at 325 nm

The luminescence spectra were measured for samples with three different Ag concentrations, 0.1 mol %, 0.2 mol %, 0.5 mol % and for different annealing times, compared to a reference sample without Ag co-doping. The excitation source used was a cw HeCd laser at 325 nm. All measurements were performed under the same experimental conditions with the same sampled volume for comparison. Fig. 3 shows the selected luminescence spectra from three samples with different Ag concentrations and annealing times: (a) PL from the sample with 0.1 mol % Ag and 24 h annealing, (b) PL from the sample with 0.2 mol % Ag and 9 h annealing, and (c) PL from the sample with 0.5 mol % Ag and 3 h annealing, all compared with a spectrum from the reference sample. Four major emission bands of Tb3+ at 489, 542, 585, and 622 nm were observed. These emission peaks are attributed to transitions of 5D4 → 7F(i = 6, 5, 4, and 3, respectively) 1. PL results in Fig. 3 illuminated the enhancement of Tb3+ luminescence in the presence of Ag NPs in glass matrix. The PL enhancement factor is 1.2, 1.9, and 2.9 for sample (a), (b), and (c), respectively. The highest PL intensity is from the sample with 0.5 mol % Ag and three h annealing time. In addition to the enhanced Tb3+ luminescence, background emission between 450 to 650 nm was observed from samples (b) and (c). This background emission increases with Ag concentration, and is therefore assumed to be from Ag related defects in the glass.

Fig. 4 shows PL enhancement factor versus different annealing times for the sample with 0.5 mol % Ag. The largest value is 2.9 for 3 h annealing and the smallest is 0.88 for 8 h annealing. The reduced PL intensity suggests a quenching effect on Tb3+ luminescence from the sample with a higher Ag concentration and longer annealing time.
Figure 3. Plasmon enhanced luminescence of Tb$^{3+}$ ions in Ag co-doped LLAS:Tb glass: (a) 0.1 mol % Ag, (b) 0.2 mol % Ag, and (c) 0.5 mol % Ag, compared with a reference sample without Ag co-doping. (325 nm excitation).

Figure 4. PL enhancement factor versus different annealing times for a glass sample with 0.5 mol % Ag (for PL peak at 542 nm and using excitation at 325 nm).
3.3 Excitation spectra

Figure 5. Excitation spectra of Ag co-doped LLAS:Tb samples: (a) 0.1 mol % Ag, 24 h, (b) 0.2 mol % Ag, 9 h, and (c) 0.5 mol % Ag, 3 h, compared with a reference sample without Ag co-doping (for emission \( ^{5}D_{4} \rightarrow ^{7}F_{3} \) at 542 nm).

Fig. 5 shows the excitation spectra for luminescence at 542 nm (\( ^{5}D_{4} \rightarrow ^{7}F_{3} \)) as the excitation wavelength tuning from 300 to 538 nm, where the spectrum (a) is from the sample with 0.1 mol % Ag and 24 h annealing, (b) is from the sample with 0.2 mol % Ag and 9 h annealing, and (c) is from the sample with 0.5 mol % Ag and 3 h annealing, each spectrum is compared to the spectrum from the reference sample without Ag. Excitation spectra demonstrate the excitation wavelength dependence of Tb\(^{3+}\) luminescence. The relative intensity from samples with Ag NPs compared to that from the reference sample reflects the combined effects of the enhancement and quenching on Tb\(^{3+}\) luminescence. Multiple excitation peaks were observed at 317, 339, 351, 368, 377, and 484 nm, which correspond to the absorption peaks of Tb\(^{3+}\) ions. Excitation spectra in Fig. 5 indicate that the luminescence of Tb\(^{3+}\) ions may increase or decrease in the presence of Ag NPs. This change in intensity is dependent on the excitation wavelength, Ag concentration, and annealing time. Excitation spectrum (a) indicates that the Tb\(^{3+}\) luminescence increases at the excitation wavelength.
between 345 to 380 nm and near 484 nm, including four resonant excitation wavelengths of 350, 367, 376, and 484 nm. Excitation spectrum (b) indicates that the Tb\(^{3+}\) luminescence increases near 325 nm, which is a non-resonant wavelength, but decreases between 345 to 385 nm. Excitation spectrum (c) indicates that the Tb\(^{3+}\) luminescence increases more significantly near 325 nm (a non-resonant wavelength), but decreases significantly between 345 to 385 nm, and near 484 nm. For all spectra, no significant Tb\(^{3+}\) luminescence was observed for the excitation wavelength near 420 nm, which is the peak of SPR of Ag 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 from metallic NPs to rare-earth ions. The effects of energy transfer between ions and particles are twofold: they may enhance luminescence by energy transfer from particles to ions and/or may quench luminescence by energy transfer from ions to particles. In our case, the light at 420 nm will certainly excite the SP of Ag NPs, but no significant Tb\(^{3+}\) luminescence was observed. This result does not support the energy transfer from Ag NPs to Tb\(^{3+}\) ions and is consistent with previous arguments by O. L. Malta, that energy transfer from the particles to the ions is not expected to be operative since the plasma lifetime is extremely short. The observed enhancement of Tb\(^{3+}\) luminescence may be attributed to LFE due to SPR of metallic NPs. According to LFE, there is an additional interaction between electromagnetic field and rare-earth ions due to the very high field gradients near a metallic particle. The local field effects may enhance absorption, emission, and energy transfer from glass host to Tb\(^{3+}\) ions. In addition, different Tb\(^{3+}\) ions are under different local field strength due to their different distance to Ag NPs, the local field could influence the Stark-splitting of Tb\(^{3+}\) energy levels and increase the inhomogeneous broadening of the excitation of Tb\(^{3+}\) ions in glass. The increased inhomogeneous broadening could result in the increased spreading of the excitation peaks, particularly near 325 nm as shown in (b) and (c). The enhanced luminescence for excitation at 325 nm could be attributed to the increased absorption and energy transfer from glass host to Tb\(^{3+}\) ions in the presence of Ag NPs. According to previous discussion, the excitation and emission wavelength, host matrix, binding state, size and shape of Ag NPs, and distance between the rare-earth ions and NPs are all important factors in LFE. The decrease of luminescence was observed for samples containing Ag NPs with higher Ag concentration of 0.2 mol % and 0.5 mol %, particularly in the excitation wavelength between 345 to 380 nm, including three resonance wavelengths of 350, 367, and 376 nm. This result suggests that quenching exceeds enhancement in this region for samples (b) and (c). The quenching effect is attributed to the energy transfer from excited Tb\(^{3+}\) ions to Ag NPs. The observed Tb\(^{3+}\) luminescence quenching is more severe for the sample with 0.5 mol % Ag and longer annealing time, which corresponds to a high particle volume fraction and large particle size of Ag NPs, consistent with previous reported results.

The observed enhancement and quenching of Tb\(^{3+}\) luminescence depends on excitation wavelength, and this dependence is further related to Ag concentration and annealing time. For sample (a) (0.1 mol % Ag, 24 h), the enhancement of PL is more significant in resonance wavelength region and closer to the peak of SPR. However, for sample (c) (0.5 mol % Ag, 3h), the enhancement of PL is observed near 325 nm, which is a non-resonant wavelength of Tb\(^{3+}\) and relatively away from SPR peak of Ag NPs, but the quenching of PL is more severe from 345 to 385 nm, and near 484 nm. It is likely that the quenching effect increases rapidly when Ag particle volume fraction or size surpassed a certain point. The exact mechanism has not yet been fully understood.

5. SUMMARY

Tb-doped Li\(_2\)O-LaF\(_3\)-Al\(_2\)O\(_3\)-SiO\(_2\) (LLAS:Tb) glasses containing different Ag concentration and annealed at different time intervals were studied. LLAS glass matrix provides a convenient host for Tb doping and for producing Ag NPs. A strong and broad absorption band centered at 420 nm due to SPR of silver NPs has been observed. The amplitude of this SPR absorption band increases systematically with annealing times. The enhancement of Tb\(^{3+}\) luminescence was observed for glass containing Ag NPs at certain excitation wavelength regions, dependent on the Ag doping concentration and annealing time. The luminescence enhancement in the presence of Ag NPs is attributed to the local field effects due to SPR of Ag NPs. Ag NPs in the glass may also participate in an observed luminescence quenching for excitation wavelengths regioning from 345 to 380 nm and 484 nm, particularly at four resonance wavelengths of Tb\(^{3+}\).
ions. This luminescence quenching is attributed to an energy transfer process from excited Tb$^{3+}$ ions to Ag NPs. The energy transfer from Tb$^{3+}$ ions to Ag NPs provides a path for extra non-radiative loss of excited Tb$^{3+}$ ions. This luminescence quenching is more significant for samples with higher Ag concentrations and longer annealing times.

ACKNOWLEDGMENTS

This research is supported by US National Science Foundation NSF-CREST- CA: HRD-0420516, NSF-STC CLiPS - grant no. 0423914, and NSF CBET-0829977.

REFERENCES