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Enhancing NIR emission of Yb^{3+} by silver nanoclusters in oxyfluoride glass

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ABSTRACT

Oxyfluoride glass comprising Yb^{3+} ions and Ag nanoclusters was prepared via a melt-quenching method. The molecule-like Ag clusters (ML-Ag) in the glass displayed broad absorption and emission bands in the ultraviolet (UV) and visible spectral regions, respectively. The luminescence quantum yield (QY) was determined to be higher than 90%. We observed energy transfer from ML-Ag nanoclusters to Yb^{3+} ions as evidenced by time resolved luminescence spectra, which resulted in a four-fold enhancement in NIR emission of Yb^{3+}. The luminescence enhancement effect described here would be applied to boost the efficiency of solar cells by converting high energy UV photons into NIR photons that better match the absorption of photovoltaic devices.

1. Introduction

In recent years, noble metal nanoparticles and nanoclusters have received considerable attention due to their unique physical, electrical, and optical properties. Especially, molecule-like silver clusters [1–4] that consist of a few to several hundred silver atoms could exhibit broad band emission, even white light emission under near-UV excitation. When embedded in hosts along with rare-earth (RE) ions, Silver nanoclusters could act as ideal sensitizer to enhance the luminescence of RE ions [5–7].

Yb^{3+} shows unique properties [8] owing to the simple energy level structure associated with $4f^{13}$ electronic configuration. Yb^{3+} displays intense and broad charge transfer band absorption, near-infrared (NIR) emission around 980 nm, and high resistance to concentration quenching. Importantly, the energy difference between the $^2F_{5/2}$ and $^2F_{7/2}$ levels of Yb^{3+} well matches the bandgap of crystalline-Si solar cells (1.12 eV) [9]. Downconversion spectral modification through use of materials activated with Yb^{3+} ions are therefore proposed to enhance the efficiency of solar cells by "concentrating" the solar spectrum into the optimum spectral response region of Si solar cells. An array of ions including Eu^{2+}, Pr^{3+}, Tb^{3+}, Ce^{3+}, and Er^{3+} have been used to sensitize the luminescence of Yb^{3+} [10–14] for such application. Herein, we describe the preparation and luminescence properties of Ag clusters and Yb^{3+} ions co-doped oxyfluoride glass. We observed efficient energy transfer from Ag clusters to Yb^{3+} ions that markedly enhances UV to NIR photon energy conversion.

2. Experimental

The glass samples were prepared by melt quenching methods and summarized in Table 1. In a typically procedure, high purity chemicals of SiO_2, Al_2O_3, ZnF_2, SrF_2, H_3BO_3, Na_2CO_3, $AgNO_3$, and YbF_3 were used as starting materials. Batches of 50 g raw materials were thoroughly mixed, placed in an electric furnace, and melted at 1450 °C for 45 min in air. Then, the melt was poured onto a copper plate, and pressed by another copper plate. The glass samples were further polished to 1 mm in thickness for optical measurements.

The optical absorption spectra were recorded on a Hitachi U-4100 UV–vis–NIR spectrophotometer. Photoluminescence spectra, quantum yield, and time resolved spectra were measured on an Edinburgh FLSP920 spectrometer equipped with a μs flash Xe lamp and a ps semiconductor pulsed lamp as excitation sources. All spectroscopic measurements were performed at room temperature.

3. Results

3.1. Optical absorption

Fig. 1 shows the optical absorption spectra of Ag/Yb^{3+} co-doped sample (GAgYb), Yb^{3+}-doped reference sample (GYb), and Ag-doped

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Table 1
Composition of the glass samples (mol%).

Sample	SiO_2	Al_2O_3	ZnF_2	SrF_2	B_2O_3	Na_2O	Ag	YbF_3
GAgYb	46.47	14.87	11.15	13.01	6.33	3.17	4.00	1.00
GAg	46.96	15.03	11.27	13.15	6.40	3.20	4.00	0
GYb	48.42	15.50	11.62	13.56	6.60	3.30	0	1.00

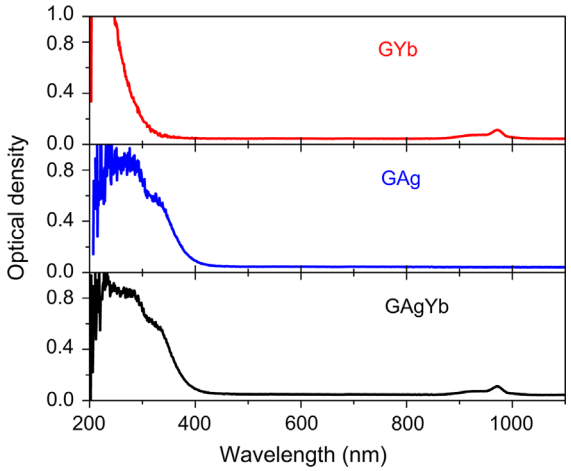

Fig. 1. Optical absorption spectra of GAgYb, GAg and GYb.

reference sample (GAg). The NIR absorption bands peaked at 974 nm for GYb and GAgYb are due to the $^2F_{7/2}$ to $^2F_{5/2}$ transition within the Yb^{3+} ions. Consistent with the same Yb^{3+} doping concentration, the optical densities are at the same level. The UV absorption edge of GYb is correlated with the band gap of the glass host. Both GAg and GAgYb have similar broad absorption band from 250 to 420 nm, which is attributed to ML-Ag in the glass host.

3.2. Photoluminescence (PL) spectra

The luminescence properties in visible (Fig. 2a) and NIR (Fig. 2b) regions were studied. Excited at 330 nm, GAg emits white light of slightly stronger intensity than that of GAgYb, while GYb shows no detectable visible emission. The visible emission peaked at 478 nm is attributed to ML-Ag and such super broad band emissions also have broad excitation band from 250 nm to 450 nm. In comparison with GAg, the visible emission of GAgYb is weakened owing to the energy transfer (ET) from Ag nanoclusters to Yb^{3+} under UV excitation.

In NIR region, GAg shows a very weak emission possibly due to ML-Ag, while both GYb and GAgYb show strong emission corresponding to $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition of Yb^{3+}. The NIR emission of GYb has an excitation band from 250 nm to 350 nm and the most effective excitation is at 272 nm for GYb, which can be ascribed to the charge transfer band from the O^{2-} coordination anions to the central Yb^{3+}. By contrast, GAgYb gets the most intense emission under 330 nm excitation and the NIR emission of Yb^{3+} is enhanced by four times, suggesting ET processes from the ML-Ag to the Yb^{3+} ions.

3.3. Luminescence dynamics

The luminescence decays of Yb^{3+} (Fig. 3a, excitation @330 nm; monitored @980 nm) are well fitted to single exponential decay function. The luminescence decays of ML-Ag (Fig. 3b, excitation @330 nm; monitored @980 nm) are non-exponential and the mean

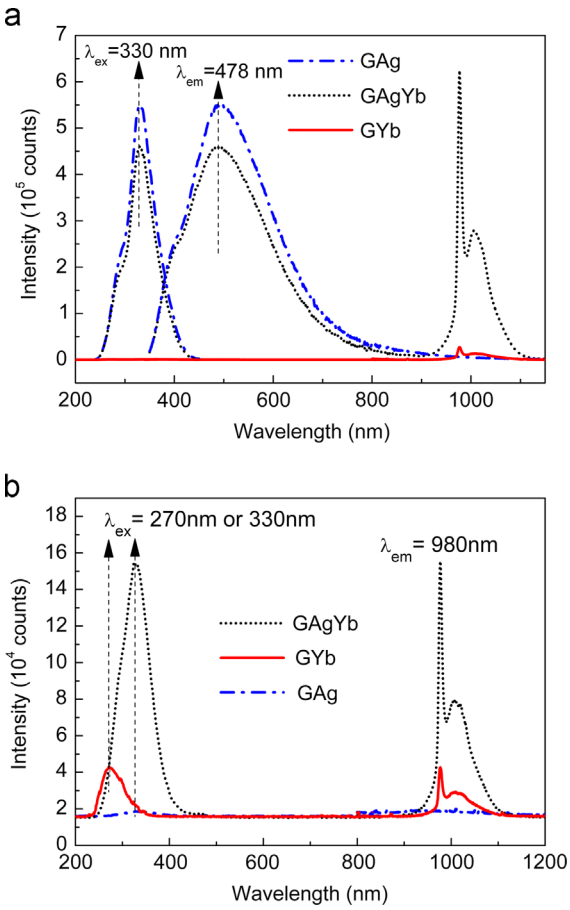

Fig. 2. Luminescence spectra: (a) visible emission, PL (exiciting at 330 nm) and PLE (monitoring at 478 nm) and (b) near-IR emission, PL (exiciting at 330 nm for GAg and GAgYb, 272 nm for GYb) and PLE (monitoring at 977 nm).

decay lifetimes are calculated by

$$\tau = \frac{\int_0^\infty I(t)t\mathrm{d}t}{\int_0^\infty I(t)\mathrm{d}t}, \quad (1)$$

where $I(t)$ is the luminescence intensity at the time t. The lifetimes of the samples are listed in Fig. 3 and reveal that GAgYb has a shorter 478 nm luminescence lifetime than GAg, confirming the ET from Ag nanoclusters to Yb^{3+}. When compared with GYb, GAgYb shows a relative slow and gradual 980 nm luminescence rising, also suggesting the involvement of ET processes.

3.4. Quantum yield (QY)

The quantum yields of GAgYb and GAg were measured using an integrating sphere (Fig. 4) and by the following equation:

$$\mathrm{QY} = \frac{\int I_{\mathrm{em}}\mathrm{d}\lambda}{\int I_0\mathrm{d}\lambda - \int I\mathrm{d}\lambda} = \frac{S_{\mathrm{em}}}{S_0 - S} \quad (2)$$

S_0–S equals to the area fenced by scatter curves of the reference $BaSO_4$ plate and the sample at the excitation region and refers to the number of absorbed excitation photons; while S_{em} is the integrated area of the emission curve and refers to the number of photons emitted by the glass sample. Under 330 nm excitation by a Xe lamp, the QYs of visible emission are calculated to be 96.75% for GAg and 82.78% for GAgYb.

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