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Dy^{3+} doped tellurite glasses containing silver nanoparticles for lighting devices

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ABSTRACT

Efficient warm yellowish-white fluorescence emissions of Dy^{3+} were observed in heavy metal germanium tellurite (HGT) glasses under the excitation of 454 nm. Further, the luminescence intensity of Dy^{3+} is increased by ~29% accompanying the introduction of Ag NPs with diameter ~7 nm when compared with that of the silver-free case, which is caused by the existence of localized surface plasmon resonance (LSPR). The larger net emission power, the more net emission photon number and the higher quantum yield in Dy_2O_3 doped HGT glasses containing Ag NPs (HGT-Ag) confirm the availability of utilizing laser. Presupposed fluorescence color trace reveals that white luminescence can be achieved when the intensity ratio between residual laser and Dy^{3+} emission reaches the appropriate range. The productive transition emissions and the tunable white fluorescence illustrate tellurite glasses embodying noble-metal NPs are a potential candidate for high-quality lighting devices.

1. Introduction

Nanometer-sized particles, usually silver and gold, have achieved widespread attentions since several fascinating properties including optical nonlinearity, thermal characteristic as well as magnetic property [1–4]. And it is usually embedded in a glass matrix with an increment in intensity of rare-earth ions [5–8], herein, an ideal sensitizer role is interpreted because of the influence of local surface plasmon resonance (LSPR) [9–14]. The combination of RE ions and silver NPs provides a hopeful direction in optical devices for laser illumination, which solves the problem of efficiency droop compared with LED phosphors [15–20].

The selection of host matrix is essential for the fabrication and development of valid optoelectronic devices and good lasing materials. Among the several glass hosts, tellurite glass is suitable for RE^{3+} ion doping thanks to its superior qualities advantages like high refractive index, low phonon energy, high transparency and possesses the capability to hold more dopant (rare earth) ions compared to the other glass hosts [21–26]. Moreover, tellurite glass host furnishes a feasible method to generate silver nanoparticles with the introduction of AgCl and further heat-treatment process. As an important member of synthetic white light, the color rendering of Dy^{3+} can be improved in tellurite glasses with the further addition of Ag NPs [27,28]. Therefore, Dy^{3+} doped tellurite glasses embodying Ag NPs are interesting subject in the optical devices [29–37].

In the present work, Dy^{3+} doped heavy metal germanium tellurite glasses (HGT) containing Ag nanoparticles are prepared after undergoing melt-quenching and post-annealing treatment, and the existence of Ag nanoparticles was further confirmed by transmission electron microscopy. Absolute characterization of glass samples emitting near-white luminescence was carried out under the excitation of 453 nm blue laser, and high quantum yields were confirmed. The results reflect that the emission intensity of Dy^{3+} in tellurite glasses was remarkably improved by the introduction of Ag nanoparticles in virtue of the LSPR, and the schematic diagram of LSPR is depicted in Fig. 1. Efficient combinatorial near-white fluorescence under the laser excitation in Dy^{3+}-doped HGT glasses containing Ag nanoparticles provides a promising orientation to develop active lighting devices.

2. Experiments

Dy^{3+}-doped heavy metal germanium tellurite glasses (HGT)

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were prepared from high purity Na_2CO_3, Bi_2O_3, PbO, GeO_2 and TeO_2 powders according to the molar host composition $2Na_2O-17Bi_2O_3-2PbO-19GeO_2-60TeO_2$. In addition, xDy_2O_3 and yAgCl with x = 0.1, 0.5, 1.0, 2.0, 3.0, y = 0 and x = 0.5, y = 0.5 as dopants were introduced in HGT glass and labeled as HGT-Dy-0.1, HGT-Dy-0.5, HGT-Dy-1.0, HGT-Dy-2.0, HGT-Dy-3.0 and HGT-Dy-0.5/Ag, respectively. The well-mixed starting materials in alumina crucibles were put into electric furnace at 880 °C for 20min, and then quenched onto an aluminum plate. The HGT-Dy and HGT-Dy-0.5/Ag glasses were subsequently annealed at 320 °C for 2 h to eliminate internal stress, and cooled down slowly to room temperature. Further, the HGT-Dy-0.5/Ag glasses were heat-treated at 350 °C for 2 h, then marked as HGT-Dy-0.5/AgH. For optical measurements, the glass samples were sliced and polished into pieces with two parallel sides.

The densities of HGT-Dy-0.5 glasses and HGT-Dy-0.5/AgH glasses were measured to be 6.113 and 6.120 g cm^{-3}, and thus the number densities of Dy^{3+} were calculated to be 9.821×10^{19} and 9.832×10^{19} cm^{-3}, respectively. Using the Metricon 2010 prism coupler, the refractive indices of HGT-Dy-0.5 and HGT-Dy-0.5/AgH glass samples were identified to be 2.0943 and 2.0951 at 635.96 nm, and 2.0333 and 2.0328 at 1546.9 nm, respectively. The refractive indices at other wavelengths can be calculated by Cauchy's equation $n = A + B/\lambda^2$ with $A = 2.0209$ and $B = 29690$ nm^2 for HGT-Dy-0.5 glasses, and $A' = 2.0201$ and $B' = 30322$ nm^2 for HGT-Dy-0.5/AgH glasses. The absorption spectra were recorded using a Perkin Elmer UV-VIS-NIR Lambda 750 spectrophotometer. Visible fluorescence spectra were measured by a Hitachi F-7000 fluorescence spectrophotometer. A 200 kV JEM-2100 transmission electron microscope (TEM) which functioned with selected area electron diffraction (SAED) was used to investigate the nucleation of silver nanoparticles in the glasses. Specimens for TEM images were prepared by dispersing the grinded glass powder in ethanol using the ultrasonic bath.

The spectral power distributions of glass samples were measured using an integrating sphere (Labsphere) with 3.3-inch diameter which was connected to a CCD detector (Ocean Optics, QE65000) with 600 μm-core optical fiber, and a 453 nm laser pigtailed with 400 μm-core fiber was used as the pump source. All the above measurements were carried out at room temperature.

3. Results and discussion

3.1. Formation of silver nanoparticles

Fig. 2(a) and (b) present the measured transmission electron microscopy (TEM) images for parallel scale of HGT-Dy-0.5/Ag and HGT-Dy-0.5/AgH glass samples. A small amount of metallic Ag has been emerged in HGT-Dy-0.5/Ag glass owing to the process of annealing, and the more metal particles are obtained in the HGT-Dy-0.5/AgH glasses with the implementation of heat-treated process for 2 h at 350 °C. The refined details of HGT-Dy-0.5/Ag and HGT-Dy-0.5/AgH glasses are investigated by adopting the larger scale of 50 nm, as shown in Fig. 2(c) and (d), which illustrates the generation of Ag nanoparticles with diameters about ~7 nm. To confirm the nucleation of Ag NPs, the SAED patterns were performed as shown in Fig. 2(e) and (f), in which the white spots in first, second and third rings are originated from the (111), (200) and (220) crystal plane reflections of metallic Ag NPs, respectively [38,39], directly proving the presence of metallic Ag in HGT-Dy-0.5/AgH glass.

It should be noticed that the formation of Ag^+ particles to Ag^0 NPs happens from two representative reactions during the high-temperature melting process [40]

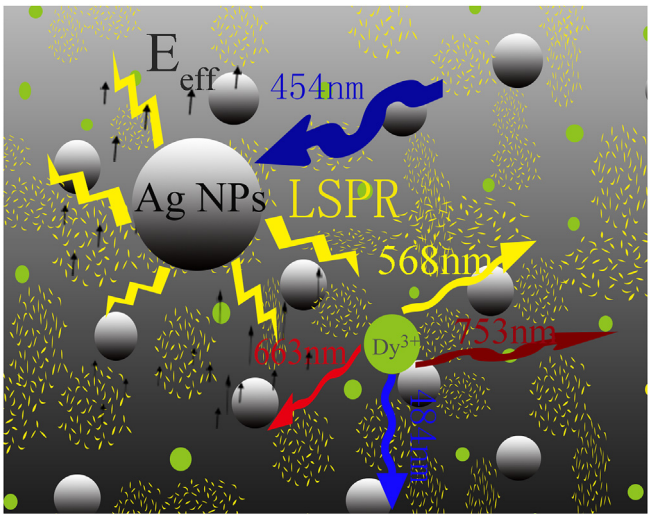

Fig. 1. Schematic diagram of localized surface plasmon resonance (LSPR).

$$Ag^+ + e^- \rightarrow Ag^0,\ Ag^+ + Ag^+ \rightarrow Ag^{2+} + Ag^0. \quad (1)$$

Furthermore, a probable mechanism of selective thermochemical reduction from in Ag^+ ions to Ag^0 atoms by Te^{4+} ions in tellurite glasses is considered as the electromotive force values or reduction potentials of the respective redox system elements, as [41]

$$Ag^+ / Ag^0 = 0.799\ V,\ Te^{6+} / Te^{4+} = 1.020\ V. \quad (2)$$

According to the above reduction processes, following process is likely to occur

$$Te^{4+} + 2Ag^+ \rightarrow Te^{6+} + 2Ag^0,\ \Delta E^0 = 0.578V, \quad (3)$$

where ΔE^0 is the total potential of reduction process. The viable reaction is Eq. (3) (with $\Delta E^0 > 0$), which illustrates the presence of silver NPs in the glass system. Meanwhile, a fraction of Ag particles can still be remained as Ag^+ ions, Ag^0 atoms, and multimers in the glass samples [42,43].

3.2. Luminescence features

Fig. 3(a) gives the typical emission spectra of Dy^{3+} doped HGT glasses with various concentrations. Under the excitation of 454 nm, Dy^{3+} possesses a variety of level transitions from $^4F_{9/2}$, and the emission spectra exhibit two visible emission peaks at approximately 483 and 575 nm corresponding to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions, respectively [44–46]. Fig. 3(b) presents the excitation spectra of Dy^{3+} in HGT glasses with different concentrations. A group of excitation bands are observed between 300 and 500 nm with the six excitation peaks at 353, 368, 392, 428, 454 and 475 nm whose are assigned to the transitions from the ground state $^6H_{15/2}$ to the various excited states of Dy^{3+} ions [47,48]. With the increment of Dy^{3+} concentration, the emission intensity and excitability of Dy^{3+} are strengthened obviously at the beginning, and the tendency becomes stagnant when the Dy_2O_3 doping concentration exceeds 2.0wt%.

To experimentally reflect the effects of Ag nanoparticles on luminescent properties in Dy^{3+} doped HGT glasses, the HGT-Dy-0.5, HGT-Dy-0.5/Ag and HGT-Dy-0.5/AgH glass samples are ground and polished, and then the emission spectra of which are compared under the same excitation conditions as shown in Fig. 3(c). The emission intensities of Dy^{3+} are increased by ~8.7% and ~29.4% in