Enhancement of dual-broadband NIR emissions in Ag NPs embedded tellurite glass doped with $Er^{3+}/Tm^{3+}/Ho^{3+}$ ions*

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Tellurite glasses combined with metal silver nanoparticles (Ag NPs) and $Er^{3+}/Tm^{3+}/Ho^{3+}$ ions were synthesized using melting and quenching technique, and the enhanced two-band near-infrared (NIR) fluorescence induced by Ag NPs was reported. Upon the excitation of 808 nm laser diode (LD), dual-broadband and flat NIR fluorescence ranging from 1 350 nm to 1 600 nm and from 1 600 nm to 2 200 nm with full width at half maximum (*FWHM*) of 154 nm and 374 nm respectively in Ag NPs embedded tellurite glass doped with appropriate concentrations of $Er^{3+}/Tm^{3+}/Ho^{3+}$ ions has an obvious enhancement of about 40% with respect to the glass sample without Ag NPs, which is attributed to the local field effect caused by Ag NPs and energy transfer from Ag species to rare-earth ions. The enhanced dual-broadband and flat NIR fluorescence enables us to develop various NIR band photonic devices flexibly.
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In many fields such as optical communication, remote sensing, environmental monitoring and laser surgery, near-infrared (NIR) band lasing source can find important applications. Therefore, in the past decades, a series of NIR band photoluminescences with different wavelength ranges have been developed through a variety of rare-earth doped schemes[1-5]. However, most of the reported NIR luminescence up to now is mainly focused on the single broadband emission and also the emission intensity is unsatisfactory, which limits their application range. Obviously, whether from the application perspective or from the application flexibility, developing intense as well as multi-band broadband luminescence is of greater significance.

Coupling of rare-earth ions with metal nanoparticles (NPs) such as metal Ag NPs has been confirmed to be an effective strategy to improve the radiative transition probability owing to the enhanced local electric field (LEF) effect induced by NPs and energy transfer from Ag species to rare-earth ions[6,7]. In this work, the metal Ag NPs were introduced into $Er^{3+}/Tm^{3+}/Ho^{3+}$ tri-doped tellurite glass to achieve two-band broadband NIR emissions and their luminescence enhancement. Under the excitation of 808 nm laser diode (LD), dual-broadband flat NIR emissions enhance greatly in tri-doped glass after introducing Ag NPs. The broadband and flat dual-band luminescence properties as well as fluorescence enhanced mechanism was investigated. Owing to its excellent physic-chemical and optical properties, such as high rare-earth solubility, high refractive index (~2.0), wide transmission region (0.35—5 μm) and low maximum phonon energy (~750 cm^{-1}), tellurite glass is a promising rare-earth doped host applied for fiber amplifier and laser.

The melting and quenching technique was performed to synthesize $Er^{3+}/Tm^{3+}/Ho^{3+}$ tri-doped tellurite glasses with metal Ag NPs for mol% compositions of $(64.05\text{-}x)TeO_2\text{-}15ZnO\text{-}10Bi_2O_3\text{-}10WO_3\text{-}0.1Er_2O_3\text{-}0.8Tm_2O_3\text{-}0.05Ho_2O_3\text{-}x$AgCl ($x$=0, 0.6, 0.9 and 1.2), and named as ETHA0, ETHA0.6, ETHA0.9 and ETHA1.2 respectively. Batches of 14 g high purity (99.99%) powder mixture was weighed accurately first. Next, the crucible with weighed mixture was heated in an electric furnace at 900 °C for 40 min. After, the melt was poured to the silica mold preheated at 320 °C and instantly transferred into annealing furnace kept at 410 °C for 8 h to remove thermal stress as well as to reduce Ag^+ ions into Ag^0 atoms and then to crystallize and grow into metal Ag NPs. Finally, the glass sample was cooled slowly to room temperature and polished for following measurements. The X-ray diffraction (XRD) pattern of glass sample was obtained by a Bruker D8 advance power diffractometer. The Ag NPs image inside glass was captured by a 2100 JEOL transmission electron microscopy (TEM). The absorption spectrum of doped rare-earth ions was measured by a LAMBDA 950 UV/Vis/NIR spectrophotome-

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ter, and the fluorescence emission signal was collected by a FLSP920 spectrometer upon the excitation of 808 nm LD.

The absorption transitions of tri-doped $Er^{3+}/Tm^{3+}/Ho^{3+}$ ions from the ground states ($^4I_{15/2}$, $^3H_6$ and $^5I_8$) to their respective excited levels in tellurite glasses with different amounts of Ag NPs are displayed in Fig.1 of absorption spectra. In the spectral range of 400—2 200 nm, no obvious changes of the peak position, shape and intensity for all absorption bands in different glass samples are found, which indicates that the effect of Ag NPs embedding on the absorption transitions of doped ions is little. Also, the absorption band of surface plasmon resonance (SPR) related to Ag NPs is not identified in these glasses, mainly due to the Ag NPs concentration is not enough to generate a noticeable SPR peak which is thus covered by the intense rare-earth absorption bands, because the existence of Ag species in glass can be in various states such as Ag^0, Ag^+, neutral or charged dimmers and multimers[8,9]. To monitor the SPR band, the absorption spectrum of no rare-earth doped tellurite glass ($64.1TeO_2$-$15ZnO$-$10Bi_2O_3$-$10WO_3$-$0.9AgCl$) but with 0.9 mol% AgCl is presented in inset of Fig.1, in which a weak SPR absorption band appears from 470 nm to 510 nm.

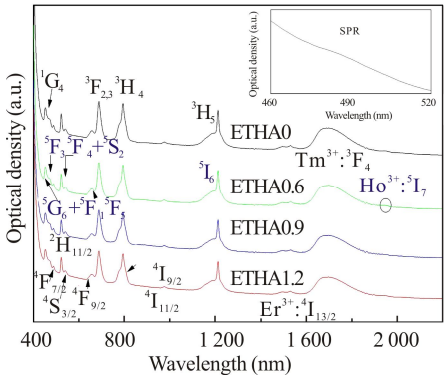

Fig.1 Absorption spectra of tri-doped tellurite glasses with different Ag NPs amounts (The inset shows the SPR band of Ag NPs)

The TEM image of Fig.2(a) measured from the $Er^{3+}/Tm^{3+}/Ho^{3+}$ tri-doped tellurite glass of sample ETHA1.2 as a representative can also confirm the existence of Ag NPs. The dark particles exhibited in image clearly indicate the presence of near-spherical Ag NPs dispersed in glass with average diameter about 10 nm. During the melting and subsequent annealing process, some of Ag^+ ions decomposed from AgCl compound are converted to Ag^0 atoms and then crystallized into Ag NPs through the thermo-chemical reduction reactions[8]. Finally, different sizes and shapes of Ag NPs are formed following the Ostwald ripening mechanism[10]. The broad hump but no sharp diffraction peaks exhibited in Fig.2(b) of the XRD patterns of $Er^{3+}/Tm^{3+}/Ho^{3+}$ tri-doped tellurite glasses demonstrated their amorphous structural nature. It can also be observed that the intensity of patterns in all glass samples is slightly different, and the possible reason is that the glass samples have a different degree of amorphousity[11].

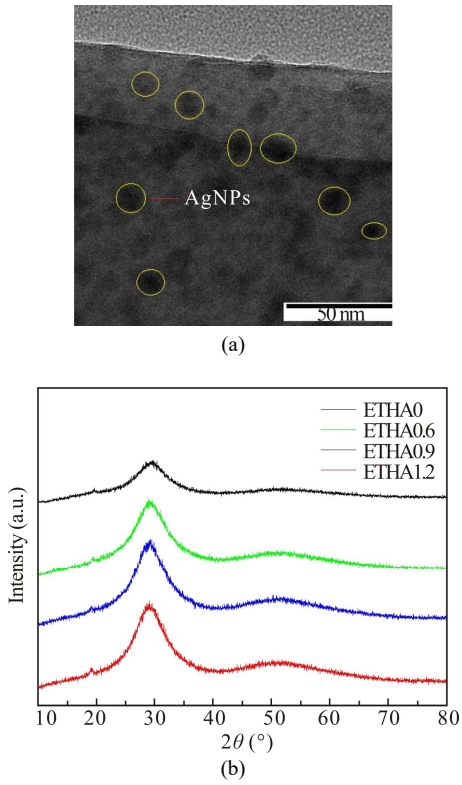

Fig.2 (a) TEM image and (b) XRD patterns of the $Er^{3+}/Tm^{3+}/Ho^{3+}$ tri-doped tellurite glasses

Fig.3 displays the NIR photoluminescence spectra in the 1 200—2 200 nm range of $Er^{3+}/Tm^{3+}/Ho^{3+}$ tri-doped tellurite glasses with different amounts of Ag NPs under the 808 nm LD excitation. In the studied wavelength range, dual-broadband and flat luminescence bands within 1 350—1 600 nm and 1 600—2 200 nm respectively are observed. Among them, the former is contributed by the spectral overlapping of 1.53 μm band of Er^{3+}: $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition and 1.47 μm band of Tm^{3+}: $^3H_4\rightarrow{}^3F_4$ transition[2,3]. This broadband luminescence band spans the low-loss region of silica fiber and the full width at half maximum (*FWHM*) is about 154 nm in the glass sample with 0.1 mol% Er_2O_3, 0.8 mol% Tm_2O_3 and 0.05 mol% Ho_2O_3 tri-doped combination. This *FWHM* is superior to the results of Er^{3+}/Tm^{3+} co-doped silica fiber[12], germanate glass[13], tellurite glass[14] and comparable with that of tellurite unclad fiber[15]. While the 1 600—2 200 nm band of the latter is contributed by the spectral overlapping of 1.85 μm band of Tm^{3+} and 2.0 μm band of Ho^{3+}, originating from the $^3F_4\rightarrow{}^3H_6$ and $^5I_7\rightarrow{}^5I_8$ transitions respectively[2,16]. The *FWHM* of this broadband luminescence band is up to 374 nm, which is larger than the results reported so far with Tm^{3+}/Ho^{3+} combination[5,17,18]. Furthermore, with the embedding

of Ag NPs, the NIR luminescence intensity enhances greatly and reaches the maximum in the $Er^{3+}/Tm^{3+}/Ho^{3+}$ tri-doped glass sample containing 1.2 mol% AgCl, which is about 40% enhancement for this two NIR bands with respect to the glass sample without Ag NPs. The enhancement of luminescence is attributed to the local field effect induced by Ag NPs, and energy transfer from Ag species which act as the sensitizers for rare-earth ions[6,7]. Fig.4 displays the energy level diagram summarizing the near-infrared band luminescence mechanisms discussed in above.

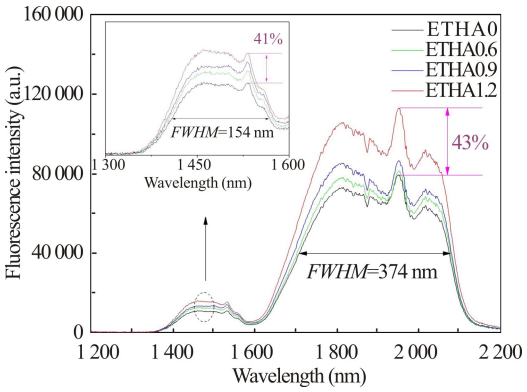

Fig.3 Photoluminescence spectra of $Er^{3+}/Tm^{3+}/Ho^{3+}$ tri-doped tellurite glasses with different Ag NPs amounts under the 808 nm excitation

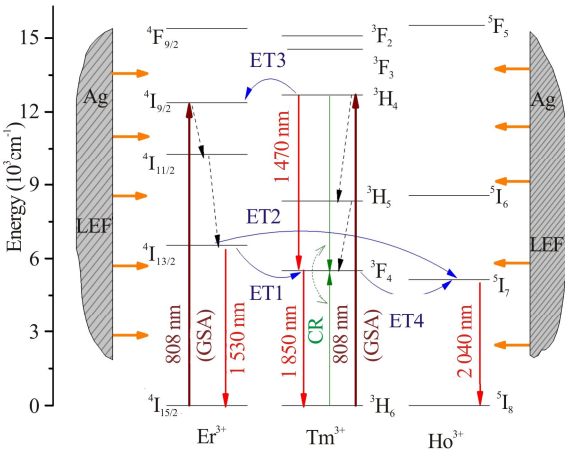

Fig.4 Energy level schematic diagram of Er^{3+}, Tm^{3+} and Ho^{3+} related with NIR emissions and the interaction between rare-earth ions and Ag NPs under the excitation of 808 nm

In summary, dual-broadband and flat NIR luminescence bands (1 350—1 600 nm, *FWHM*=154 nm) and (1 600—2 200 nm, *FWHM*=374 nm) were obtained in tellurite glass with 0.1 mol% Er_2O_3, 0.8 mol% Tm_2O_3 and 0.05 mol% Ho_2O_3 combination under the excitation of 808 nm LD, and underwent an enhancement of about 40% after introducing Ag NPs with average diameter about 10 nm. The enhanced broad flat dual-band NIR emissions are promising in the flexible fabrication of photonic devices such as broadband amplifiers and tunable lasers.

Statements and Declarations

The authors declare that there are no conflicts of interest related to this article.

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