Suppression of second-order cooperative up-conversion in Er/Yb silicate glass

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1. Introduction

Erbium (Er) doped waveguide amplifiers (EDWAs) have attracted increasing attention in recent years with the rapid development of photonics. As a critical component, EDWAs can compensate the losses occurring in other functional devices such as splitters, modulators and waveguides. Various materials and methods have been used to fabricate EDWAs [1–10]. In these reported approaches, due to the insolubility of Er in host material, the Er concentration is around \(10^{20}/\text{cm}^3\) [11–15]. However, the increase of Er concentration does not mean successful approach of high-gain compact amplifiers for the purpose of on-chip integration use, higher Er concentration and Er peak emission cross-section. Under same 1480 nm pump power, Er/Yb silicate glass shows 4.7 times weaker visible up-conversion luminescence and four times stronger infrared luminescence than Er/Y silicate glass. Through analyzing the physical mechanism, we found that the energy back transfer from Er to Yb plays a significant role on the luminescence difference, which affects and further suppresses the second-order CUC process in Er/Yb co-doped materials.

This paper reports the efforts of suppressing Er ion’s second-order cooperative up-conversion (CUC). Er/Yb and Er/Y silicate glass waveguides were fabricated, which have same structure, similar Er concentration and peak emission cross-section. Under same 1480 nm pump power, Er/Yb silicate glass shows 4.7 times weaker visible up-conversion luminescence and four times stronger infrared luminescence than Er/Y silicate glass. Through analyzing the physical mechanism, we found that the energy back transfer from Er to Yb plays a significant role on the luminescence difference, which affects and further suppresses the second-order CUC process in Er/Yb co-doped materials.
2. Experiment

In the experiment, the active films were fabricated by the radio frequency (RF) magnetron sputtering method. Two mixed targets, which are mixture of Er2O3, Y2O3 (or Yb2O3), and SiO2 powders with a mol ratio of 1:9:10, were sputtered by argon ions at a pressure of 3 m Torr. The RF powers applied on the target is 100 W. The sputtered films have a thickness of about 550 nm determined by ellipsometer measurement and cross-sectional scanning electronic microscope (SEM) images, which are annealed for 30 min at 750 °C. Then 620-nm-thick SiO2 was deposited on them by plasma enhanced chemical vapor deposition (PECVD) method. Through photolithography and etching, 500-nm-deep and 2.4-μm-wide SiO2 stripes were fabricated. To confirm the composition of the sputtered films, Rutherford back scattering spectrometry (RBS) measurement was carried using 2.022 MeV He+ ions with a detection angle of 165°, plus X-ray fluorescence spectra (XRF) measurement for the discrimination of Er and Yb. The ellipsometer measurement from 190 nm to 830 nm was executed to determined the refractive index and the thickness of the deposited films. The refractive index at infrared wavelength range is a fitted result according to the measured data. To get the absorption spectra, a tunable laser with wavelength range of 1440–1640 nm was used as a signal light source. A polarization controller was employed to ensure the light to be transverse-electric (TE) mode propagating along the waveguides. In the measurement, fiber-coupled 1480 nm continuous wave laser was used as pumping source. A multimode fiber was placed vertically above the sample surface to collect the scattered light, which was dispersed by an iHR550 monochromator followed by a lock-in amplifier for light intensity measurement. Here, it should be noted that the pumping schema from the ground state to the metastable state of Er3+ using 1480 nm source is more appropriate for fluorides and tellurite glasses than for silicates, because the former possess lower phonon energy [22].

3. Result and discussion

To confirm the composition of the sputtered films, RBS measurement was executed, which is shown in Fig. 1. The black curves are the measured results and the red lines are the fitted ones. For Er/Y silicate glass as shown in Fig. 1a, the simulation gives a composition of Er:Y:Si:O = 1:7.1:4.2:29.4, which is slightly different from the stoichiometric value of the target of Er0.2Y1.8SiO5. For Er/Yb silicate glass as shown in Fig. 1b, due to similar atomic weight of these two elements (Er:167.3; Yb:173), the energy resolution of the RBS spectrum (~30 keV) is insufficient to separate the contributions from Yb and Er. Therefore, we sum the contributions of the Yb and Er ions in the RBS spectrum, which gives a result of (Er + Yb)2SiO7. As an additional method, XRF measurement was carried out, which demonstrates the ratio of Er to Yb of 1:7.2. As a result, the composition of Er/Yb silicate glass is Er:Yb:Si:O = 1:7.2:4.1:28.7. From the measurements, we can see that these two materials have nearly same Er mol content. The mol contents for other elements are also comparable. The atomic volume concentrations of Er in the two films are calculated by dividing the Er areal density determined from RBS by the film thickness obtained from SEM images. The values are 1.55 × 1021 cm−2 and 1.41 × 1021 cm−3 for Er/Y silicate glass and Er/Yb silicate glass, respectively.

Fig. 2 shows the measured absorption spectra for the fabricated waveguides at wavelength range from 1500 nm to 1580 nm. The black curve is for the 6.2-mm-long Er/Y silicate glass waveguide and the red one is for the 5.7-mm-long Er/Yb silicate glass waveguide. The Er absorption at 1640 nm is weak and can be neglected. For these two waveguides, the absorption losses at 1580 nm are both about 1.5 dB. The maximum absorptions appear at 1533 nm and are 15.43 dB and 15.97 dB for Er/Y and Er/Yb silicate glass waveguides, respectively.

The refractive indexes of these two kinds of silicate glass are both about 1.65 fitted from the data by ellipsometer measurement. Given the index of 1.45 for SiO2, the confinement factor Λ for the fundamental TE mode is calculated to be 0.7. The waveguide absorption loss can be written as $\alpha_{abs} = \Gamma \times \sigma_{abs} \times N_{tot} \times L$, where $\sigma_{abs}$ is the absorption cross-section, $N_{tot}$ is the total Er concentration and L is the waveguide length. At 1533 nm, $\alpha_{abs}$, $\Gamma$, $N_{tot}$, L are 15.43 dB (3.55 cm−1), 0.7, 1.55 × 1021/cm3, 0.62 cm for Er/Y silicate glass.
waveguide, and 15.97 dB (3.68 cm⁻¹), 0.7, 1.41 × 10⁻²¹/cm³, 0.57 cm for Er/Yb silicate glass waveguide, respectively. Thus we can get the peak Er absorption cross-section as σ_{abs} = 5.28 × 10⁻²¹ cm² for Er/Y silicate glass and σ_{abs} = 6.54 × 10⁻²¹ cm² for Er/Yb silicate glass which are equal to the peak emission cross-sections. The emission cross-sections are slightly smaller than the reported value of 0.9 × 10⁻²⁰ cm² in Er/Y silicate waveguide [20].

Fig. 3 shows the infrared luminescence spectra under 274 mW pumping, which were measured by collecting the scattering light above the tested waveguides. The two materials have same PL peak at 1533 nm and similar line shape due to the same annealing temperature. At the peak position of 1533 nm, the intensity for Er/Yb silicate glass (red line) is about four times stronger than that of Er/Y silicate glass (black line). Based on the reality of similar waveguide structure, annealing condition, Er concentration and Er emission cross-section at 1533 nm, the PL intensity difference comes from the different dopants of Y and Yb in Er silicate glass. It seems that Yb can help to promote Er ion’s infrared luminescence in Er/Yb silicate glass compared with Y in Er/Y silicate glass. At 980 nm wavelength, the PL intensity is very weak and comparable for these two silicate glass.

Up-conversion luminescence spectra at visible wavelength range were measured, which are shown in Fig. 4. Under the same pump power of 274 mW, these two waveguides show completely different up-conversion spectrum lineshapes. The black curve is for Er/Y silicate glass waveguide, which has several peaks distributing at 410 nm (ultraviolet light), 524 nm (green light), 550 nm (green light) and 660 nm (red light). For Er/Y silicate glass waveguide, the emission at 660 nm is about eight times weaker than that at 550 nm. The up-conversion spectrum for Er/Yb silicate glass is the red curve with only a single peak at 660 nm. The integrated intensity in the visible range for Er/Yb silicate glass is 4.7 times weaker than that for Er/Y silicate glass. In the measurement, green light emission was observed along the as-fabricated Er/Y silicate glass waveguide, which is shown in the inset (a) of Fig. 4. Comparatively, because of the absence of green light emission, a red line was observed along Er/Yb silicate glass waveguide [23], which is shown in the inset (b) of Fig. 4.

To further analyze the up-conversion properties, the dependence of 1533 nm, 980 nm, and 550 nm intensities on pump power in log–log plot for these two materials was depicted in Fig. 5. Fig. 5a shows that these two materials have nearly same slope of 0.82 and 0.83 for 1533 nm luminescence on pump power. It suggests that the Er;4I_{11/2} based up-conversion is nearly not affected by different dopants of Y and Yb. Fig. 5b is the dependence of 980 nm intensity on pump power. The slope is 1.31 for Er/Yb silicate glass and 1.02 for Er/Y silicate glass. The smaller slope for Er/Y silicate glass means larger influence of up-conversion on 4I_{11/2} state than that in Er/Yb silicate glass [24]. Fig. 5c gives the slopes of the 550 nm intensity on pump power, which are 2.23 for Er/Y silicate glass and 1.87 for Er/Y silicate glass. The smaller slope in Er/Y silicate glass than in Er/Yb silicate glass suggests more serious up-conversion in Er/Y silicate glass than in Er/Yb silicate glass [24]. From Fig. 5, we can see that in the present pump power region, up-conversion intensity is suppressed in Er/Yb silicate glass compared with that in Er/Y silicate glass.

The different luminescence means different physical mechanisms in these two materials under 1480 nm pumping. For the Er/Y silicate glass, Y³⁺ only plays a neutral role of separating Er³⁺ and will not participate in the 1533 nm luminescence and up-conversion process. The observed green light emission can be described by the second-order CUC and excited state absorption (ESA) processes [19]. Just as shown in Fig. 6a-i, the first CUC process happens to two Er ions on the 4I_{11/2} state and brings one ion to the 4I_{9/2} state. Then the rapid nonradiative transition from 4I_{9/2} populates 4I_{11/2} state. The 4I_{11/2} state second-order CUC process populates 2H_{11/2} state, which is shown in Fig. 6a-ii. Radiative transition from the 2H_{11/2} state to the ground state explains the 524 nm light emission. Nonradiative transition from the 2H_{11/2} state populates the 2S_{3/2} and 4F_{9/2} states, which can emit 550 nm and 660 nm light, respectively. Furthermore, Er ions on the 4I_{11/2} state can also jump to the 4F_{9/2} state by absorbing 1480 nm pumping photons, which is known as ESA process.

Besides the same up-conversion mechanism to Er/Y silicate glass, an addition mechanism plays a significant role for the suppressed up-conversion in Er/Yb silicate glass. According to the RBS result, the ratio of Er concentration (N_{Er}) to Yb concentration (N_{Yb}) is about 1:7. In addition, the Er ion population on ground state 4I_{15/2} (N_0) and the first excited state 4I_{13/2} (N_{1}) is larger than that on 4I_{11/2} state (N_2). Thus N_2 is far smaller than N_0 (N_2 ≪ N_0). Under this situation, the energy back transfer from Er: 4I_{11/2} ions to Yb ions has priority to energy transfer between two excited Er ions on 4I_{11/2} state. The excited Yb ions have more chance to transfer their energy to Er ions on 4I_{11/2} and 4I_{13/2} states than those on 4I_{11/2} state. For clarity, the energy transfer route between Er ions and Yb ions can be described by Fig. 6b-i. The Er ions on 4I_{11/2} state transfer their energy to Yb ions. Then the excited Yb ions directionally transfer their energy to Er ions on 4I_{15/2} and 4I_{13/2} states. Therefore, just as shown in Fig. 6b-ii, the 4I_{11/2} state based second-order...
CUC process is largely constrained due to the decreased population on \( ^{4}I_{11/2} \) state. As a result, the emission peaks at 524 nm and 550 nm in Fig. 4 nearly disappear. Furthermore, the energy transfer from excited Yb ions to Er ions on \( ^{4}I_{13/2} \) populates Er: \( ^{4}F_{9/2} \) state, which emits 660 nm red light by radiative transition to the ground state. This Yb participated energy transfer up-conversion (ETU) and \( ^{4}I_{11/2} \) based ESA explain the 660 nm emission [23].

From the above analysis, it can be seen that, though the ratio Er:Yb = 1:7.2 in the Er/Yb silicate glass is similar to the ratio Er:Y = 1:7.1 in Er/Y silicate glass, the visible upconversion luminescence is much different. For Er/Y silicate glass, due to the first-order CUC process, the population on the \( ^{4}I_{11/2} \) state is relatively large, which contributes the stronger second-order up-conversion process. Comparatively, for the Er/Yb silicate glass, the population on the \( ^{4}I_{11/2} \) state is limited because of the energy back transfer from Er\(^{3+}:^{4}I_{11/2}\) to Yb\(^{3+}:^{2}F_{7/2}\), which result in the suppressed second-order up-conversion process and weakened visible luminescence.

4. Conclusion

Er/Yb and Er/Y waveguides with similar structure, Er concentration and Er emission cross-section were fabricated. Though Y and Yb ions have the same role of separating neighbored Er ions in these two materials under 1480 nm pumping, the resonant energy level at 980 nm actually affects the up-conversion process, which induces the energy back transfer from Er: \( ^{4}I_{11/2} \) state to Yb: \( ^{2}F_{7/2} \) state and further results in the decreased second-order CUC process. Due to this physical mechanism, suppressed up-conversion was observed in Er/Yb silicate glass compared with Er/Y silicate glass under the same 1480 nm pump power. The strong second CUC process in Er/Y silicate glass leads to relatively strong 550 nm light emission and visible green light along the fabricated waveguide. Comparatively the emission peaks at 550 nm and 524 nm nearly disappear in Er/Yb silicate material due to the suppressed second-order up-conversion and red light can be easily observed along the waveguide.

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