Er^{3+} -doped phosphor-tellurite glass for broadband short-length Er^{3+} -doped fiber amplifier

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 Er^{3+} -doped phosphor-tellurite glass for broadband short-length Er^{3+} -doped fiber amplifier (EDFA) is fabricated and characterized. The differential value (ΔT) of onset crystalline temperature (T_x) and glass transition temperature (T_g) is 206 °C. The stimulated emission cross section of Er^{3+} is calculated from absorption spectrum by McCumber theory and is 0.87×10^{-20} cm² at 1532 nm. A broad 1.5- μ m fluorescence spectrum with 54-nm full-width at half maximum (FWHM) is demonstrated. Especially, the maximum phonon energy of undoped phosphor-tellurite glass is 1100 cm⁻¹, which restricts the upconversion luminescence. It is possible to pump efficiently at 980 nm. These results indicate Er^{3+} -doped phosphor-tellurite glass is suitable for fabricating broadband short-length EDFA.

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Er³⁺-doped tellurite glasses are promising host materials for broadband and flat gain optical amplifier applications to improve transmission capacity of wavelength division multiplexing (WDM) system^[1,2]. By now, Er^{3+} -doped tellurite glass fiber amplifier with net gain of 20 dB at 1530 - 1610 nm and noise figure smaller than 6.5 dB has been reported^[3]. Compared with 1480-nm pumping scheme, 980-nm pumping scheme could provide full population inversion and a good value of signal-to-noise ratio. So adoption of 980-nm pumping scheme is essential. In order to obtain a high gain within an optical fiber or optical waveguide in the length of centimeters, the heavy doping of erbium ions in glass is necessary. The phonon energy of tellurite glass is relatively low (< 800 cm^{-1}) as a result that its upconversion fluorescence is very strong and its pumping efficiency is low at 980-nm pumping scheme. On the other hand, the glass transition temperature of tellurite glass is also relatively low (about 300 °C), which makes it liable to thermal damage at high optical intensities. Many works have been done for the sake of overcoming these defects. Oxides such as WO_3 , B_2O_3 , CeO_2 , and Eu_2O_3 have been added into glass in order to improve the performance of tellurite glasses^[4-7]. Among these kinds of glasses, Er^{3+} -doped phosphor-tellurite glasses which have higher phonon energy and higher glass transition temperature and can be heavily doped, were rarely reported^[8]. In this article, thermal stability and spectroscopic properties of Er^{3+} doped phosphor-tellurite glass is discussed.

Glass with molar composition of 50%TeO₂-20%ZnO-5%Nb₂O₅-5%BaO-5%WO₃-15%P₂O₅ doped with 0.5 wt.-% Er₂O₃ was prepared. Glass sample was melted using high purity raw materials in a quartz crucible at 850 °C. The melted glass was poured into a preheated steel mold, and immediately transferred to a preheated furnace and annealed at about glass transition temperature. Two big surfaces of glass sample with a dimension of $30 \times 15 \times 2$ (mm) were polished to high optical quality and used for the following experiments. The density of the glass was determined by the Archimedes methods with distilled water as the immersion fluid. The absorption spectrum was recorded with a Perkin-Elmer 900 spectrophotometer over a spectral range of 350 - 1700 nm. The fluorescence spectrum in the range of 1400 - 1700 nm were measured with a Jobin-Yvon Frolog3 spectrofluorimeter upon excitation at 980 nm. The fluorescence lifetime for the ${}^4I_{13/2}$ level of Er^{3+} was measured with light pulses of 980-nm laser diode (LD) and a HP546800B 100-MHz oscilloscope. The glass transition temperature (T_g) and onset crystallization temperature (T_x) were analyzed with NETZSCH DTA409 PC/PG at a heating rate of 10 K/min. Thermal expansion coefficient of glass sample was measured on PCY-1 dilatometer at a heating rate of 10 K/min from room temperature to the soft-point. Raman spectrum was determined from Lambda DP1 Raman spectrometer from $200 \text{ to } 1500 \text{ cm}^{-1}$. All measurements were taken at room temperature.

As far as the optical fiber loss is concerned, it is known that the estimated intrinsic losses of tellurite glasses are at most comparable to silica glass. However, extrinsic losses from microcrystal formed during heating and quenching cycles in the perform process and fiber fabrication usually dominate the fiber loss, unless the glass possesses a high thermal stability. The $T_{\rm g}$ and $T_{\rm x}$ of ${\rm Er}^{3+}$ -doped phosphor-tellurite glass were 418 and 624 °C, respectively. $\Delta T = T_{\rm x} - T_{\rm g}$ is commonly used to evaluate thermal stability of glasses from the characteristic temperatures. The desirable ΔT for fiber drawing is understood to be greater than 100 °C. The ΔT value here is 206 °C. Obviously, Er³⁺-doped phosphor-tellurite glass possesses high ΔT and is very suitable for fiber drawing process. The thermal expansion coefficient was $1.173 \times 10^{-5} \text{ K}^{-1}$, which is much smaller than the value of previous tellurite glass $(1.469 \times 10^{-5} \text{ K}^{-1})^{[9]}$ and comparable to that of Schott phosphate glass IOG-1 $(1.123 \times 10^{-5} \text{ K}^{-1})^{[10]}$.

According to absorption spectrum, the absorption cross section $\sigma_{\rm a}(\lambda)$ of ${\rm Er}^{3+}$ ions was determined. The peak absorption cross section of ${\rm Er}^{3+}$ -doped phosphor-tellurite

glass is around 0.77×10^{-20} cm² at 1531 nm. The stimulated emission cross section $\sigma_{\rm e}(\lambda)$ is calculated from McCumber theory^[11]. Figure 1 illustrates the calculated absorption and stimulated emission cross sections of ${\rm Er}^{3+}$ ions and the maximum stimulated emission cross section is 0.87×10^{-20} cm² at 1532 nm. The high stimulated emission cross section of ${\rm Er}^{3+}$ -doped phosphor-tellurite glass is due to the high value of refractive index n, since the stimulated emission cross section of rare earth ions is proportional to the refractive index of glass matrix $[\sigma \sim (n^2 + 2)^2/n]^{[12]}$.

Figure 2 shows the emission fluorescence spectrum of Er^{3+} in phosphor-tellurite glasses. Because of the difference of the emission spectra in different glass hosts, the full-width at half maximum (FWHM) is often used as a semi-quantitative indicator of the bandwidth. The FWHM for Er^{3+} -doped phosphor-tellurite glass is 54 nm, which is larger than those of phosphate glasses and silicate glasses. The measured fluorescence lifetime of ${}^{4}I_{13/2}$ level of Er^{3+} is 3.0 ms, which is comparable to other tellurite glasses^[13].

Figure 3 shows the Raman spectrum of undoped phosphor-tellurite glass. The band at 475 cm⁻¹ is ascribed to the symmetrical stretching or bending vibrations of Te – O – Te linkages^[12]. The bands around 685 and 756 cm⁻¹ are attributed to TeO₄ trigonal bipyramid (tbp) units and TeO₃ trigonal pyramid (tp) units, respectively^[14]. The band at 917 cm⁻¹ is due to the stretching vibrations of W = O and W–O⁻ bonds associated with WO₄ and WO₆ groups^[4]. The broad band from 980 to 1250 cm⁻¹ (peak value 1100 cm⁻¹) is assigned to the symmetrical stretching vibrations of the PO₄



Fig. 1. Absorption and stimulated emission cross sections of Er^{3+} in phosphor-tellurite glass.



Fig. 2. Fluorescence spectrum of Er^{3+} -doped phosphortellurite glass.



Fig. 3. Raman spectrum of undoped phosphor-tellurite glass.

tetrahedra with two non-bridging oxygens^[15,16]. The energy gap of transition ${}^{4}I_{11/2} \rightarrow {}^{4}I_{13/2}$ is about 3600 cm⁻¹ and the lifetime τ of the ${}^{4}I_{11/2}$ level in oxide glasses is determined almost entirely by the non-radiative decay rate $W_{\rm n}$, which can be estimated from an empirical formula^[17]:

$$\tau^{-1} = W_{\rm n} = C \exp[-(\Delta E - 2\hbar\omega)\alpha],\tag{1}$$

where C and α are the characteristic parameters of the glass-type but independent of the specific electronic level of rare earth ions from which the decay occurs. For tellurite glass, C and α were given as $10^{7.97} \,\mathrm{s}^{-1}$ and 4.7×10^{-3} , respectively^[18]. ΔE and $\hbar \omega$ are the energy gap and photon energy of the host, respectively. According to Eq. (1), the lifetime of the ${}^{4}I_{11/2}$ level of phosphor-tellurite glass is 7.7 μ s, which is much smaller than the lifetime (207.3 μ s) of the ${}^{4}I_{11/2}$ level in 75TeO₂-20ZnO-5Na₂O glass ($\hbar \omega = 750 \,\mathrm{cm}^{-1}$). So it is possible to efficiently pump at 980 nm. In fact, no obvious upconversion luminescence was detected at the pump power of 500 mW, which indicated that the introduction of high phonon energy oxide P₂O₅ increased the non-radiative decay rate of Er³⁺ ions and reduced the upconversion luminescence.

In conclusion, Er^{3+} -doped phosphor-tellurite glass has high thermal stability, large absorption and stimulated emission cross sections, and a broad emission width with 54-nm FWHM. The improvement of the maximum phonon energy of phosphor-tellurite glass reduces the intensity of upconversion luminescence, which makes the pumping efficient under 980-nm pumping scheme. Consequently, Er^{3+} -doped phosphor-tellurite glass can be used as a potential host material for developing broadband short-length erbium-doped fiber amplifier (EDFA) in WDM.

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