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2–3 μm emission and fluorescent decaying behavior in Ho^{3+}-doped tellurium germanate glass

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ABSTRACT

In this work, we report the 2.05 μm emission and ~3 μm broadband spectra of Ho_2O_3-doped $33GeO_2$–$30TeO_2$–27PbO–10CaO (in mol%) glass under 640 nm laser excitation. Clear emission spectra due to the $^5I_7$–$^5I_8$ transition and the $^5I_6$–$^5I_7$ transition in Ho^{3+} are observed. The 2.05 μm emission intensity and the full width at half maximum (FWHM) of the ~3 μm broadband depend on the Ho concentration. The peak stimulated emission cross-section of Ho^{3+} is 6.57×10^{-21} cm^2 at 2.05 μm, as calculated by the McCumber theory. The emission spectra are recorded and the maximum emission intensity at 2.05 μm is obtained at a doping level of 0.5 mol% Ho_2O_3 in the glass. A broad and flat emission band from 2700 nm to 3050 nm is observed in 2 mol% Ho_2O_3-doped tellurium germanate glass. The lifetime of the $^5I_7$ state decreases with the increase in Ho^{3+} concentration due to non-radiative relaxation processes. An energy transfer coefficient of 271.88 mol^{-1} s^{-1} is obtained.

1. Introduction

Due to their potential applications in medicine, remote sensing, and atmospheric pollutant monitoring [1–4], fiber lasers at wavelengths around 2 μm have become the object of significant research activities. Singly-doped Tm and Ho, as well as co-doped Tm:Ho systems, have been investigated for this purpose. Although the "two-for-one" process of Tm^{3+} is regarded as helpful to the generation of photons in the 2 μm region, the theoretical efficiency of these systems is not as high as it is for the resonant pump mechanism of Ho-doped glass fibers. Additionally, direct pumping of Ho^{3+}-doped lasers can offer the possibility of reaching longer wavelengths and high short-pulse extraction efficiently [5]. Ho^{3+} is also a potential candidate for 3 μm laser output. In 1999, Tetsumi et al. [6] demonstrated highly efficient and high-power continuous-wave cascade oscillation with a holmium ion-doped ZBLAN glass fiber with simultaneous oscillation wavelengths of 3 and 2 μm. The water absorption peaks at 3 and 2 μm are about 10^4 cm^{-1} and 10 cm^{-1} respectively, which indicates the Ho-doped glass fiber could have applications in the medical field. However, studies on the mid-infrared spectra of Ho^{3+}-doped glasses are limited by the lack of an appropriate pump source. As is shown by Boyer et al. and Huang [7,8], Ho^{3+} possesses an absorption band around 640 nm. As such, a pump source with a wavelength of 640 nm was used in this research.

In this paper, tellurium germanate glass was chosen as the host material. It is known that germanate glass has robust mechanical qualities, with a lower phonon energy than silica glass. Compared to germanate glass, TeO_2-based glass possesses lower phonon energy and higher refractive index, which are beneficial for radiative transitions of Ho^{3+} ions. However, the poor thermo-mechanical properties of tellurite glass limit its applications. By selecting a suitable combination of these two glasses, it may be possible to obtain ideal optical properties of Ho^{3+} while maintaining good thermal and mechanical characteristics. However, to the best of our knowledge, reports on the 2 and 3 μm emission properties of Ho^{3+}-doped tellurium germanate glass are limited.

In this work, the spectroscopic characteristics of Ho^{3+}-doped tellurium germanate glass samples were investigated. In order to develop Ho-doped tellurium germanate glasses or fibers for applications in ~2 μm lasers, the identification of the optimum Ho^{3+} concentration in the system was considered.

2. Experimental details

Ho^{3+}-doped tellurium germanate glasses of molar composition: $33GeO_2$–$30TeO_2$–27PbO–10CaO–xHo_2O_3, where x = 0.01, 0.1, 0.25, 0.5, 1 and 2 mol%, were used. Accurately weighted 20 g batches

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of raw materials were fully mixed and then melted at 800 °C, followed by quenching in air. The samples were annealed for 5 h at the glass transition temperature and then cooled to room temperature. The samples were subsequently cut and carefully polished to a size of 15 × 15 × 1 mm^3 and used for optical measurements.

Electronic absorption spectra of the glass samples were measured in the 300–2100 nm region at room temperature using a Perkin Elmer Lambda 900UV/VIS/NIR spectrophotometer. The emission spectra of the bulk glasses were measured with a Triax 320 type spectrometer (Jobin–Yvon Co, France) after excitation with 640 nm lasers. The prism minimum deviation and Archimedes methods were utilized to measure the refractive index and density, using distilled water as the immersion liquid. For the lifetime measurements of the Ho^{3+}: $^5I_7$ state, an FLSP 920 (Edinburgh Instruments Ltd, UK) was used. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Absorption spectra and Judd–Ofelt analysis

The room temperature absorption spectra were obtained for all glass samples between 300 and 2100 nm. The spectra of all the samples are similar, and the absorption spectrum of the 2 mol% Ho_2O_3-doped glass sample is shown in Fig.1 as an example. The primary absorption bands of Ho^{3+} are labeled in the figure. Notably, no clear ~800 nm absorption band was observed in the glass sample, which indicates that commercially available LD with a wavelength 808 nm cannot be used as the pump source for a Ho^{3+} single-doped matrix. The integrated absorption intensity of the $^5I_7$–$^5I_8$ transition at different Ho_2O_3 concentrations is presented in the inset of Fig. 1. The strong linearity indicates that there is no cluster phenomenon occurring among Ho^{3+} ions [9].

The Judd–Ofelt (J–O) theory [10,11] has been used to estimate the intensities of the intraconfigurational f–f transitions of RE^{3+} ions. According to the theory, the transition intensities are characterized by three J–O intensity parameters, Ω_t (t = 2, 4, and 6), which depend on the local environment around the rare earth ions. The J–O parameters, particularly Ω_2, are closely related to the glass composition. Ω_2 is sensitive to the symmetry of the rare earth sites and covalency between rare earth ions and ligand ions. Ω_2 will increase with increasing asymmetry and covalency. In oxide glasses, Ω_6 is more sensitive to the overlap integral of the 4f and 5d orbitals which dominate the transition probability of the f–f transition

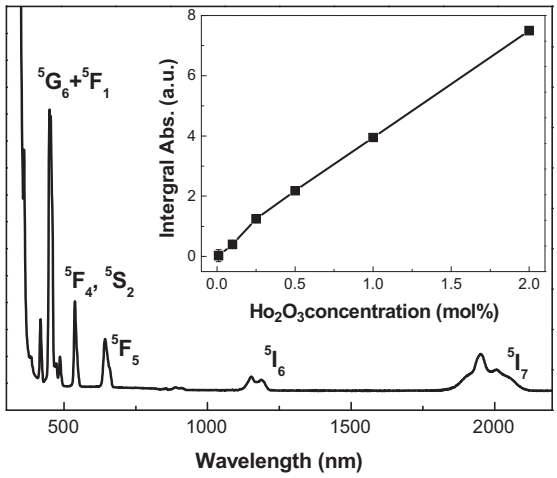

Fig. 1. Absorption spectrum of tellurium germanate glass with 2 mol% Ho_2O_3. Inset: the integrated absorption intensity of $^5I_7$–$^5I_8$ transition at various Ho_2O_3 concentrations.

[12]. Table 1 shows that the covalency of the rare earth-oxygen (Ho–O) band in tellurium germanate glass is stronger than in tellurite glass, oxyfluoride tellurite glass, and alkali-germanate glass, but lower than gallo-germanate glass. As the Ho^{3+}: $^5I_7$–$^5I_8$ transition is mainly affected by Ω_6 [13], the tellurium germanate glass in this study should have a higher radiative transition probability (A) than in oxyfluoride tellurite and alkali germanate glass.

The radiative transition probability (A), radiative lifetime (τ_{rad}), and branching ratio (β), which predict the fluorescence intensity of the lasing transition, have been calculated using Ω_t parameters along with the refractive index (n) [18]. Table 2 shows the spontaneous emission, branching ratios, and calculated radiative lifetimes for the main emitting states of Ho^{3+} ions. The spontaneous emission probabilities of $^5I_7$–$^5I_8$ and $^5I_6$–$^5I_7$ of Ho^{3+} are 130.19 s^{-1}, and 39.94 s^{-1}, which are higher than in germanate glass, silicate glass, and fluoride glass [17]. This may be related to the higher refractive index. The increase in radiative transition probability usually leads to a stronger luminescence intensity in the corresponding glass.

3.2. Absorption and emission cross-sections

The absorption cross-section of the $^5I_8$–$^5I_7$ transition of Ho^{3+} ions can be calculated by the equation:

$$\sigma_a(\lambda) = \frac{2.303}{Nl} OD(\lambda) \quad (1)$$

where $OD(\lambda)$ is the optical density of the measured absorption spectrum, N is the concentration of the Ho^{3+} ions (ions/cm^3), and l is the thickness of the glass samples.

In materials acting as hosts for lasers, the stimulated emission cross-section is an important property that has to be determined. When no saturation effects or no excited state absorption are present, emission cross-section is defined as the intensity gain of a laser beam per unit of population inversion, which is extremely useful to determine the possibility of achieving laser effects. The stimulated emission cross-section is calculated by the McCumber theory [19,20] for Ho^{3+} as:

$$\sigma_e(\lambda) = \sigma_a(\lambda) \frac{Z_l}{Z_u} \exp\left[\frac{hc}{kT}\left(\frac{1}{\lambda_{lu}} - \frac{1}{\lambda}\right)\right] \quad (2)$$

where $\sigma_a(\lambda)$ is the absorption cross-section, h is the Planck constant, c is the light speed. T is the temperature, and k is the Boltzmann constant. Z_l and Z_u are the partition functions for the lower and upper levels, respectively. λ_{lu} is the wavelength corresponding to the zero line energy, which is the difference between the lowest Stark multiples of the high and low energy levels. The absorption and stimulated emission cross-sections are shown in Fig. 2. As can be seen in the figure, the peak stimulated emission cross-section of Ho^{3+}-doped tellurium germanate glass is 6.57 × 10^{-21} cm^2 at 2.05 μm, which is larger than silicate glass and fluoride glass [17]. The larger stimulated emission cross-section is mainly due to the high refractive index of the glass matrix and the high spontaneous transition probability, which are beneficial to the laser output of Ho^{3+}-doped tellurium germanate glass fiber [21].

Table 1
Judd–Ofelt parameters of Ho^{3+} in different glass systems.

Glass	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	Ω_6 (10^{-20} cm^2)
Tellurite [14]	4.98	0.99	2.96
Oxyfluoride tellurite [15]	4.2	2.8	1.1
Gallo-Germanate [16]	6.66 ± 0.07	6.06 ± 0.11	2.26 ± 0.09
Alkali-germanate [17]	3.30	1.14	0.17
This work	5.5	3.6	1.19