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Preparation and investigation of Tm^{3+}/Ho^{3+} co-doped germanate-tellurite glass as promising materials for ultrashort pulse laser

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ABSTRACT

The Tm^{3+}/Ho^{3+} co-doped germanate-tellurite glasses with good thermal properties were prepared. A flat emission with full width at half maximum (FWHM) = 373 nm at ~2 μm was observed in the prepared glass upon the 808 nm excitation. Besides, the cross-sections of the prepared glass have been calculated, and the relative small peak absorption cross-sections (σ_{abs}) corresponding to the Ho^{3+}: $^5I_7 \rightarrow {}^5I_8$ is the factor to obtain the flat emission. Moreover, the energy transfer microscopic parameters (C_{DA}) between RE^{3+} ions have been investigated and quantitatively explained the observation of the flat and broadband emission. Furthermore, when P = 0.2, the gain coefficient becomes positive which indicates the prepared glasses possess superior gain ability. The results indicate that the prepared glasses could be promising candidate for ~2 μm tunable or ultrashort pulse laser materials.

1. Introduction

In recent years, ~2 μm continuous wave and pulse lasers have attracted considerable attention because of its potential applications in the eye-safe lasers, atmospheric pollution monitoring, remote sensing and military countermeasure [1–5]. Additionally, compared with ~1 μm ultrashort pulse laser which is already commercialized, ~2 μm ultrashort pulse laser is more propitious to some commercial and scientific applications including micromachining, spectroscopy and pumping nonlinear frequency conversion processes [6]. Fiber-based sources of ultrashort pulses have some well-known advantages of compactness and environmental reliability compared to other solid state lasers.

~2 μm fiber lasers are generally obtained in Tm^{3+} or Ho^{3+} doped glass fiber owing to the transition of Tm^{3+}: $^3F_4 \rightarrow {}^3H_6$ and Ho^{3+}: $^5I_7 \rightarrow {}^5I_8$, respectively [7–11]. Tm^{3+} is a suitable laser active ion because of its large stimulated emission cross section, high quantum efficiency and the strong absorption band around 808 nm Tm^{3+} doped glass fiber usually has a broad amplification band of about 300 nm at ~2 μm supporting generation of femtosecond pulses and wide tunability. Compared with Tm^{3+} ion, both the emission cross section and the fluorescence lifetime of Ho^{3+} ion are superior over it. However, lacking of readily available LD pumping source limits the development of Ho^{3+}-doped fiber laser. Fortunately, this problem can be solved by co-doping other ions as sensitize ions. On the other hand, according to the uncertainty principle, the laser pulse bandwidth is limited by the bandwidth of the amplification band. Therefore, to obtain the ultrashort pulse laser, the amplification spectrum band should be as broad as possible, because the shorter the pulse lasts, the broader band will be needed. Besides, a broad amplification band supports the generating of wide tunability. Hence, great attention has been paid to the Tm^{3+}/Ho^{3+} co-doped researches because Tm^{3+} can be used as sensitize ions and Tm^{3+}/Ho^{3+} co-doped gain medium usually has a broad gain band which can reach to 400 nm [12–14].

Because silicate glasses (including silica glass here) have a good thermal stability and high damage threshold, the ~2 μm fiber laser host materials mainly focused on silicate glasses [15–17]. Naturally, ~2 μm ultrashort pulse laser was obtained firstly in silicate glass [17,18]. However, the major problem of silicate glass is the high phonon energy (~1000 cm^{-1}), which causes a high probability of nonradiative transition, limiting its emission efficiency. Moreover, the amplified spontaneous emission band of RE^{3+} doped silicate glass is narrow and uneven. These disadvantages limit its further application in ~2 μm ultrashort pulse laser. As yet, a picosecond level ~2 μm laser pulse has already been realized in silicate glass

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fiber without pulse compressor [10] and hundreds femtosecond level ~2 μm laser pulse has been obtained in silicate glass fiber with all fiber internal pulse compressor [18]. To our best knowledge, there is no report on ~2 μm laser with shorter pulse width in silicate glass fiber. Thus, to achieve shorter ultrashort laser pulse in fiber, the heavy-metal oxide glasses [19–22], such as germanate glass and tellurite glass, have become a new hotspot of research. Germanate glass has attracted a lot of interests not only for its good chemical durability, the high glass transition temperature (~600 °C) to resist thermal damage at high pumping power, but also for its low phonon energy (~900 cm^{-1}) [23]. Compared with germanate glass, the tellurite glass has much lower phonon energy (~760 cm^{-1}), which can reduce the multi-phonon relaxation rate of the doped rare earth ions [24]. In 2010, the 410 fs and 630 fs pulse duration of ~2 μm pulse laser has been obtained in Tm^{3+} doped fluo-germanate glass fiber and Tm^{3+}/Ho^{3+} co-doped tellurite glass fiber, respectively [25]. But both the fluo-germanate and tellurite glass have poor thermal stability corresponding to their low glass transition temperature (~350–450 °C). In this work, the germanate-tellurite glass was selected as host glass material, because it combines the advantages of germanate and tellurite glass, such as the better thermal stability and chemical durability, higher glass transition temperature, lower phonon energy and higher transparency [26]. So, the germanate-tellurite glass could be a relatively ideal host material for ~2 μm tunable laser or ultrashort pulse laser.

In this work, a series of germanate-tellurite glasses have been prepared. The thermal properties were investigated via the differential scanning calorimeter (DSC). The radiative properties of the Tm^{3+} and Ho^{3+} of the prepared glasses were evaluated according to the J-O theory and M-C theory. Moreover, an intense broadband emission at ~2 μm is obtained upon the 808 nm LD excitation. To further evaluate the broadband emission performance of the prepared glass, the glass with the optimum full width at half maximum (FWHM) was selected to discuss the cross section and gain coefficient. The results verify that the Tm^{3+}/Ho^{3+} co-doped germanate-tellurite glasses could be potential materials for mid-infrared broadband lasers.

2. Experimental

The glasses composed of $70GeO_2$-$10TeO_2$-$20(K_2O$-Nb_2O_5-$La_2O_3)$. (mol%) were prepared by traditional melt-quenching method with using high-purity (≥99.99%). The glasses were doped with *x* mol% Tm_2O_3 and *y* mol% Ho_2O_3 (x = 1; y = 0, 0.1, 0.2, 0.3, 0.5 and x = 0; y = 0.5). The well-mixed 20 g batches of samples were placed in Al_2O_3 crucible and heated with a SiC-resistance electric furnace at 1200 °C for 25 min. The melts were then poured onto a preheated stainless mold, followed by annealing at 500 °C for 4 h to relinquish the inner stresses. After that, it was allowed to cool slowly to room temperature. The annealed samples were cut and polished into a shape of 20 × 20 × 1.6 mm^3 for optical measurements.

The density of samples (4.27) were tested by Archimedes principle using distilled water as an immersion liquid with error limit of ±0.05%. Refractive indexes (1.73) were measured by prism minimum deviation method at the wavelength of 1053 nm. The vitreous and/or crystalline nature of the glasses were identified by X-ray diffractometer (XRD) with Cu-Kα radiation (λ = 1.5406 Å) at 40 kV tube voltage and 40 mA tube current. The glass transition temperature (T_g), crystallization onset temperature (T_x) and crystallization peak temperature (T_p) were characterized by a NETZSCH DTA 404 PC differential scanning calorimeter at a heating rate of 10 K/min with error of ±5 °C. Absorption spectra were recorded with a Perkin-Elmer-Lambda 900 UV/VIS/NIR spectrophotometer in the range of 300–2200 nm. Photoluminescence spectra in the range of 1500–2400 nm were determined by a liquid-nitrogen-cooled PbS detector using an 808 nm laser diode (LD) as an excitation source. The same experimental conditions for different samples were maintained so as to get comparable results. All the measurements were performed at ambient temperature.

3. Results and discussions

3.1. Thermal stability

The characteristic temperature (the temperature of glass transition T_g, temperature of onset crystallization T_x and temperature of peak crystallization T_p) of the prepared glass was determined through the differential scanning calorimeter (Netzsch) curves as shown in Fig. 1. T_g is an important factor for laser glass, a higher one (540 °C) which is higher than that of tellurite (354 °C) [27], bismuth (365 °C) [28] and comparable to germanate glass (556 °C) [29] means the prepared glass has a strong resistance to the thermal damage at high pumping power. ΔT (T_x-T_g) is another factor to evaluate the glass thermal properties, and a larger ΔT indicates the glass possesses an excellent thermal ability against the nucleation and crystallization. The ΔT (180 °C) of the prepared glass is larger than that of tellurite [21], germanate [19]. Therefore, the prepared glass has good resistance to devitrification after the formation of the glass and might have potential application in fiber laser.

3.2. Absorption spectra and J-O analysis

The absorption spectra of the Tm^{3+} singly doped, Ho^{3+} singly doped, Tm^{3+}/Ho^{3+}-codoped samples at room temperature in the wavelength region of 300–2200 nm are shown in Fig. 2. For Ho^{3+} singly doped sample, absorption bands centered at 1948, 1152, 900, 645, 539, 487, 452 and 419 nm correspond to the transitions starting from the ground state $^5I_8$ to excited levels $^5I_7$, $^5I_6$, $^5F_5$, ($^5F_4$ + $^5S_2$), ($^5F_{2,3}$ + $^3K_8$), ($^5G_6$ + $^5F_1$) and $^5G_5$, respectively. It can be seen that the shape and the peak positions of each transition in Ho^{3+}-doped germanate-tellurite glass are very similar to those in other Ho^{3+}-doped glasses [30–32]. But there is no absorption peak at 808 nm, so the Ho^{3+}-doped glasses cannot be pumped by 808 nm laser diode (LD). For the Tm^{3+}-doped sample, the absorption spectrum is characterized by five bands at 1704, 1210, 791, 685 and 460 nm, which can be assigned to the transitions from the $^3H_6$ ground state to the $^3F_4$, $^3H_5$, $^3H_4$, $^3F_{2,3}$ and $^1G_4$ excited states,

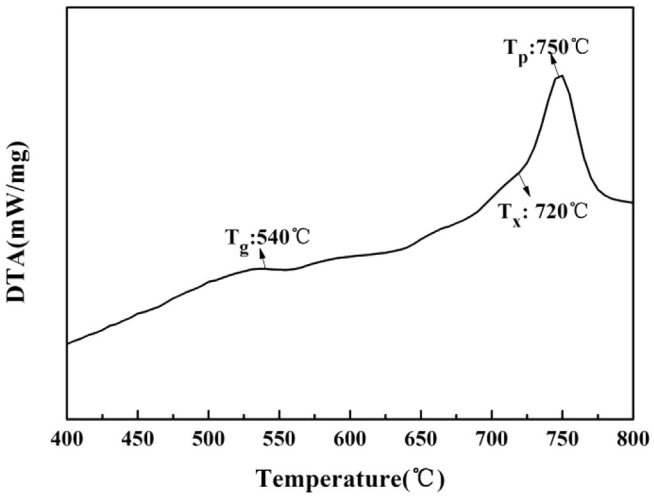

Fig. 1. DSC curves of germanate-tellurite glass.