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Emission properties of Er^{3+}-doped $Ge_{20}Ga_5Sb_{10}Se_{65}$ glasses in near- and mid-infrared

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HIGHLIGHTS

- The glasses maintains a good solubility for Er ions.
- The glasses showed a good thermal stability, heat treatment has no significant effect on the transmission in the mid- and far-infrared.
- The fluorescence intensity in the annealed glasses is increased about 7 times than that in the based glasses.

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ABSTRACT

In this work, we reported the fabrications and characterization of Er^{3+}-doped $Ge_{20}Ga_5Sb_{10}Se_{65}$ glasses and glass-ceramics and measured their transmission and fluorescence spectra. The results showed that, the fluorecence intensity of the glasses increased until Er^{3+} concentration was up to ~1.1 wt% Er, and then decreased with further increasing Er^{3+} concentration that was due to concentration quenching effect. While it was found that the mid- and far-infrared transmission did not decrease significantly in the glasses annealed at 310 °C for a duration up to 50 h, seven-folded enhancement in the intensity of mid-infrared fluorescence at 2.78 μm was observed. This demonstrated the potentials of the materials used for Er-doped amplifier and fiber laser.

1. Introduction

Amorphous chalcogenides doped with rare-earth ions (REI) are promising in various applications, such as optical fiber amplifiers [1], optical waveguides [2], sensors and detectors [3–5], trichromatic (RGB) display devices [6], laser devices [7,8]. Chalcogenide glass (ChG)-based nonlinear optical waveguides have proven to be very useful for high-speed all-optical signal processing of telecommunications signals [9–12]. However, there are also a significant propagation loss in chalcogenide optical waveguides [13]. Thus, a method of overcoming the optical losses is desirable to enhance the efficiency of all-optical processing. One approach to remedy this situation is to employ rare earth ions (REI) doped waveguides in which optical gain can compensate the propagation losses [13]. Furthermore, the lower phonon energy in ChGs reduces the impact of multi-phonon processes such as multi-phonon relaxation (MPR) or phonon-assisted parasitic transitions and considerably enhances emission cross section in ChGs. However, there is limited reports on realizing net-gain in Er-doped chalcogenide optical waveguide [14,15]. Due to the low concentration of doping rare earth ions in the chalcogenide glass, the emission efficiency is usually low in such glasses [14]. Recently it has been reported that, the addition of Ga could improve the solubility of REI in ChGs and the optimal ratio between Ga and REI was established to be ~10:1 [16,17]. In order to improve the emission efficiency, it is essential to investigate the solubility of REI in ChGs and the kinetic process of energy transfer between different energy level of REI.

The fluorescence properties of Er^{3+}-doped ChGs have been widely investigated. Several studies have reported luminescence enhancement in sulfur-based glass–ceramics in comparison to the base glass due to the presence of a crystalline environment surrounding REI [18–20]. It has been suggested that, the change in local chemical surroundings during nucleation results in a longer radiative lifetime [21]. Such crystallization effects have seldom been reported in selenide glass matrices despite the fact that selenium-based glasses provide even lower phonon energies and wider infrared (IR) transparency [22,23]. Therefore in this paper, $Ge_{20}Ga_5Sb_{10}Se_{65}$ was

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selected as a host the glass matrix, and the glasses with different concentrations of Er^{3+} were prepared. The emission properties were investigated in order to understand how the Er^{3+} concentration could affect the emission intensities. The crystallization behaviors of the $Ge_{20}Ga_5Sb_{10}Se_{65}$ glass-ceramics doped with 1.0 wt% Er^{3+} were also studied, to observe how the crystallization affect transmission and MIR fluorescence of the glass-ceramics.

2. Experimental procedure

Bulk $Ge_{20}Ga_5Sb_{10}Se_{65}$ glasses (15 g) doped with Er^{3+} (x = 0, 0.5, 0.8, 1.0, 1.1, and 1.2 wt%) were prepared by the melt-quenching method. For convenience, they were named as GGSS, GGSS-0.5Er, GGSS-0.8Er, GGSE-1.0Er, GGSS-1.1Er, and GGSS-1.2Er, respectively. High purity Ge, Ga, Sb, Se elements (99.999%) and Er elements (99.9%) were weighted and placed into silica ampule (Φ10 mm), which was evacuated to $\sim 10^{-3}$ Pa and sealed. The mixture was melt in a rocking furnace at 950 °C for 18 h, then homogenized at 850 °C for 1.5 h. The ampoules were quenched in cold water, swiftly moved into a preheated furnace to anneal at 30 °C below T_g for 5 h and then slowly cooled down to room temperature. The as-prepared glass rod was cut into several disks (Φ10 mm × 1 mm) that was further optically polished. The calorimetric measurements were carried out using differential scanning calorimetry (DSC, TA Q20 Thermal Analysis) at a heating rate of 10 °C/min with a temperature accuracy of ±1 °C. The characteristic temperatures, such as glass transition temperature (T_g), the temperature of onset crystallization (T_x), and the temperature of crystallization peak (T_p), were thus obtained. The GGSS-1.0Er glasses were heated a rate of 2 °C/min up to a designated temperature (above T_g) and held for various durations to create the glass-ceramics.

About 10 mg sample were used to examine the thermal stability of the glass using differential scanning calorimetry (DSC, TA Q20 Thermal Analysis). The absorption spectra of the samples were measured using Perkin-Elemer's Lanbda 950 UV/VIS/NIR pectrophotometer at a range of 400–2500 nm. Near- and Mid-IR fluorescence spectra in a range of 1000–4100 nm were measured via a FLS980 spectrometer (Edinburgh Instruments) equipped with a SCITEC Model 420 lock-in amplifier and an InSb detector (DInSb 55-De) cooled with liquid nitrogen. A Ti:sapphire laser (Coherent Mira 900-D) at 980 nm was used as an excitation beam. The structure of the samples was examined using a X-ray diffractometer (Bruker D2 Phaser diffractometer fitted with a linear LynxEye™ detector) with a step width of 0.01° and the possible crystalline phases precipitated in the heat-treated samples were identified via comparing with the standard JCPDF cards.

3. Results and discussion

3.1. Absorption and the near- and mid-infrared emission spectra

Absorption spectra in Fig. 1(a) shows absorption bands corresponding to Er^{3+} ions dissolved in $Ge_{20}Ga_5Sb_{10}Se_{65}$, where x = 0.5, 0.8, 1.0, 1.1, 1.2 wt%. The absorption bands are attributed to the electronic intra-4*f* transitions in Er^{3+} ions from a ground energy level $^4I_{15/2}$ to higher energy states $^{2S+1}L_J$ that are located at 1540 nm ($^4I_{15/2} \rightarrow {}^4I_{13/2}$), 990 nm ($^4I_{15/2} \rightarrow {}^4I_{11/2}$), and 810 nm ($^4I_{15/2} \rightarrow {}^4I_{9/2}$), respectively.

Near-infrared emission spectra of the GGSS glasses with different Er^{3+} concentrations were measured and the results were shown in Fig. 2(a). The fluorescence at 1.54 μm comes from the transition of $^4I_{13/2} \rightarrow {}^4I_{15/2}$. It was found that, the luminescence intensity

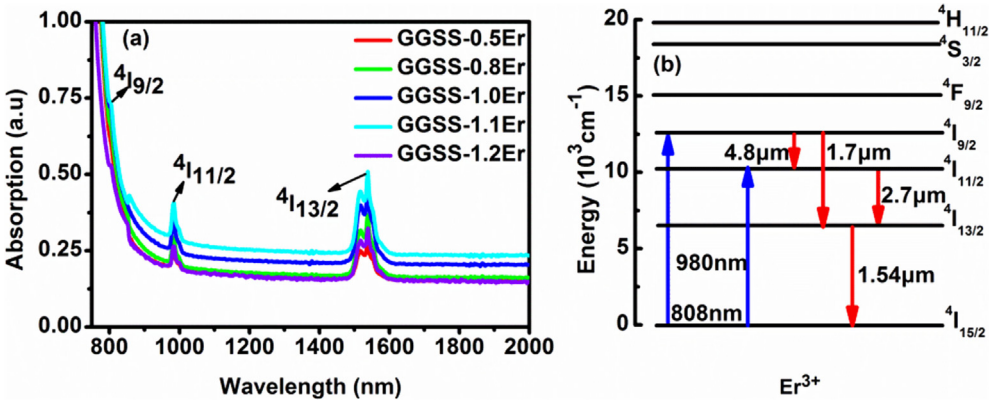

Fig. 1. (a) Absorption spectra of the glasses doped with 0.5 to 1.2 wt% Er^{3+}. (b) The energy level diagram of Er^{3+} along with pump and fluorescent transitions.

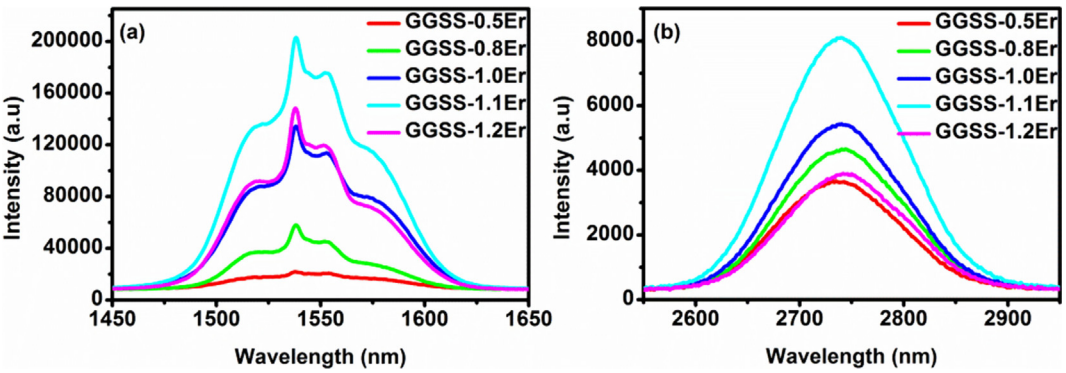

Fig. 2. (a) The near-IR and (b) mid-IR emission spectra of GGSS glasses with different Er^{3+} concentrations excited at 980 nm.