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Promising emission behavior in Pr^{3+}/In selenide-chalcogenide-glass small-core step index fiber (SIF)

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Selenide-chalcogenide glass, small-core, step-index fiber (SIF), core-doped with Pr^{3+}: 9.51×10^{24} ions m^{-3} (500 ppmw) is fabricated for the first time with indium to help solubilize Pr^{3+}. Core diameters of 20 or 40 μm are confirmed using scanning electron microscopy and near-field imaging; fibre numerical aperture is ~0.4. Optical loss is $\geq$ 4.9 dB m^{-1} across the 3–9 μm mid-infrared (MIR) spectral range. On pumping at 1.55 μm or 2.013 μm, the SIFs give broad MIR emission across 3.5–6 μm assigned to $^3H_6 \rightarrow {}^3H_5$ and $^3H_5 \rightarrow {}^3H_4$. The Pr^{3+} emission-lifetime at 4.7 μm decreases from *bulk*-glass (10.1 ± 0.3 ms), to *intermediately* processed fiber (8.10 ± 0.5 ms) to SIF (7.1 ± 0.5 ms) induced by the processing. On end-pumping SIFs at 2.013 μm, the output pump-power and emission intensity at 4.7 μm became sub-linear and super-linear, respectively, suggesting MIR excited-state saturation is occurring.

1. Introduction

The mid-infrared (MIR) spectral region spans the 3–50 μm spectral range [1]. MIR sources include blackbodies (*e.g. Globar*©), but these display low brightness. In contrast, MIR quantum cascade lasers, an emerging technology, and MIR OPOs (*optical parametric oscillators*) and gas (HeNe, CO, CO_2) lasers, which are mature technologies, exhibit high brightness. New MIR fiber narrow-line lasers are being developed along two strands: (i) nonlinear conversion, using stimulated Raman gain scattering [2] and (ii) direct-emission, rare earth ion (RE)-doped [3–6], - the topic of this study. MIR RE-doped fiber lasers have not yet been demonstrated at ≥4 μm [7], yet potentially offer advantages of compactness, high quantum efficiency, high brightness, excellent beam quality, ability to be pulsed, and greater reliability over gas lasers. MIR RE-doped fiber-lasers have prospective applications in providing new wavelengths for cutting/welding of soft materials, including polymers and in medical fiber-laser-surgery of human-tissue, and as narrow-line MIR molecular sensors [8]. Importantly, MIR RE-doped fiber lasers are potential pumps for MIR fiber supercontinuum (SC) laser sources to achieve all-fiber solutions for portable, real-time, broadband MIR molecular sensing, for instance for early diagnosis of cancer [8–15].

Chalcogenide glasses are promising RE hosts for MIR fiber-lasing due to their low phonon energy, large refractive indices hence large RE absorption/emission cross sections, long fluorescent-decay lifetimes [6] and potential for low optical-loss fiber-fabrication [see [16] and refs. therein]. Selenide-chalcogenide glasses, selected here, retain longer-wavelength near-infrared (NIR) transparency for pumping with commonly available lasers.

RE solubility is poor in binary chalcogenide glasses *e.g.* $As_{40}Se_{60}$ [17]. A Ga-solubilizer is commonly added to aid RE solubility in chalcogenide glasses [18] based on Ge-As/Sb-S/Se [18–23]. The RE solubility is considered to be enhanced by means of local [Ga-(S/Se)-RE] chemical-complexing [18]. We have made bulk selenide glasses doped with up to 6000 ppmw RE in the presence of Ga [24]. Also, with a Ga solubilizer, we have fabricated 500 ppmw Pr^{3+}/Ga small-core selenide-glass SIF (step-index fiber) which for the first time exhibited the same emission-lifetime at 4.7 μm as its parent bulk-glass - 7.8 ms [23]. This result implied that glass homogeneity was retained during the SIF glass-fabrication processing which was verified by a painstaking study to image and analyse the SIF small-core, and core/cladding interface, using high resolution transmission electron microscopy [23].

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An In solubilizer was used to make a Pr^{3+}/In bulk selenide-chalcogenide glasses and large-core SIF [25–27]. In is in the same Group of the Periodic Table, as Ga, but heavier. Thus, potentially an [In-(S/Se)-RE] chemical-complex could offer a local, lower phonon energy environment to improve RE radiative-efficiency compared to the [Ga-(S/Se)-RE] chemical-complex, notwithstanding that RE 4f inner level transitions tend to be shielded from the local chemical environment. Indeed, on pumping at 1.55 μm, we found that the Pr^{3+} emission across 3.5–6 μm, and emission at 4.7 μm, were of greater intensity, and longer lifetime, respectively, in the Pr^{3+}/In bulk glass than in the Pr^{3+}/Ga bulk glass [25]. Further work on producing high purity Pr^{3+} doped multi-component chalcogenide glasses can be found in Refs. [28–30], including the use of indium iodide to incorporate indium into Ge-As-Se-In-I [29] and Ge-Sb-Se-In-I [30] glasses.

Here, we report on a study of the emission behavior and fabrication for the first time of Pr^{3+}/In small-core SIFs based on selenide-chalcogenide glasses. The concentration of In solubilizer in the Pr^{3+}core was fixed at 1 atomic % (at. %). The SIF core-diameters were 20 μm and 40 μm, with a NA (numerical aperture) of ~0.4 (estimated from Ref. [23]) and V-parameter ~ 5.0, giving multi-moded behavior at 4–6 μm wavelength, corresponding to the $^3H_6 \rightarrow {}^3H_5$ and $^3H_5 \rightarrow {}^3H_4$ emissions and potential lasing emissions.

On pumping the SIF at 1.55 μm or 2.013 μm, broad MIR emission at 3.5–6 μm was observed. The Pr^{3+} emission-lifetime at 4.7 μm decreased from *bulk*-glass (10.1 ± 0.3 ms), to *intermediately* processed fiber (8.10 ± 0.5 ms) to SIF (7.1 ± 0.5 ms); the decrease may have been induced by the processing. On end-pumping SIFs at 2.013 μm, the output pump-power collected from the opposite fiber-end to that pumped and emission intensity at 4.7 μm collected from same fiber-end to that pumped, became sub-linear and super-linear, respectively, suggesting MIR excited-state saturation is occurring for the first time in a chalcogenide-glass fiber.

2. Experimental

2.1. Bulk glass preparation

2.1.1. Cladding-glass boule (for extrusion to tube)

A Ge-As-In-Se-S cladding-glass boule (see Fig. 1) was prepared. Ge (5n Materion), As (7n5 Furakawa Denshi, prior heat-treated at 10^{-3} Pa), indium (6n5 Alfa Aesar), Se (5n Materion, prior heat-treated at 10^{-3} Pa) and S (5 N, prior boiled under 10^{-3} Pa for 5 min) were batched inside a glovebox (MBraun: <0.1 ppm H_2O and <0.1 ppm O_2) and melted 850°C/8 h in a silica glass ampoule (prior air-baked then vacuum-baked, each 1000°C/6 h) before being quenched and annealed. 3 atomic% (at%) Se substitution by S manifested useful contrast in optical microscopic and SEM imaging; 1 at% Se replaced by S in chalcogenide glasses has been reported to reduce refractive index by 0.005 at 1.8 μm [31]. Glasses were annealed at the DSC *onset*-Tg [32].

2.1.2. Core-glass rod for caning and intermediate fiber-drawing

9.51×10^{24} ions m^{-3} (500 ppmw) Pr^{3+}-doped Ge-As-In-Se host core-glass (Fig. 1) was prepared. First, Ge-As-Se was prepared as in Section 2.1.1 and the glass transferred to a silica-glass still with 500 ppmw Al-wire (5 N, Alfa Aesar: O-getter). The still was sealed under vacuum (10^{-3} Pa) and distillation executed within a two-zone furnace (Instron). The distilled Ge-As-Se was re-melted 800°C/7 h, quenched, annealed and transferred to a new silica-glass ampoule (air-baked then vacuum-baked, each at 1000°C/6 h) and re-melted with both indium (6n5 Alfa Aesar) and 500 ppmw Pr^{3+} (3n Alfa Aesar) for 6 h/850 °C to form the doped core-glass rod. Again, glasses were annealed at the DSC *onset*-Tg [32].

2.2. Extrusion, caning, fiber-drawings and SIF fabrication

The extrusion, caning, fiber-drawings and SIF fabrication are depicted in processes (a), (b), (i) and (ii), respectively, in Fig. 1:

(a) A melt-derived Ge-As-In-Se-S cladding-glass boule (from Section 2.1.1) had an outside-diameter (OD) = 28.7 ± 0.1 mm and length (L) = 17 ± 0.1 mm. This boule was extruded [33] to give a cladding-tube (non-RE-doped Ge-As-In-Se-S) of OD = 10.5 ± 0.2 mm and ID (inner diameter) = 1.95 ± 0.05 mm (see Fig. 1(a)).

(b) A melt-derived 9.51×10^{24} ions m^{-3} (500 ppmw) Pr^{3+}-doped Ge-As-In-Se core-glass rod (from Section 2.1.2) was directly caned to give unclad cane of OD = 1.5 ± 0.1 mm (see Fig. 1(b)).

(i) The melt-derived 9.51×10^{24} ions m^{-3} (500 ppmw) Pr^{3+}-Ge-As-In-Se core-glass rod (from Section 2.1.2) was directly fiberised to give unclad *intermediate*-fiber, OD = 230 μm ± 20 μm (see Fig. 1(i)).

(ii) The 9.51×10^{24} ions m^{-3} (500 ppmw) Pr^{3+}-Ge-As-In-Se unclad cane (see (b) above) was inserted in the Ge-As-In-Se-S cladding-tube (see (a) above) and then fiber-drawn as ‘rod(b)-in-tube(a)’ (under N_2 gas (BOC)) to make small-core SIF with 9.51×10^{24} ions m^{-3} (500 ppmw) Pr^{3+} doped Ge-As-In-Se core and undoped Ge-As-In-Se-S cladding, of core-OD as-designed/fiber OD = 20 μm/130 μm and = 40 μm/270 μm, respectively, (see Fig. 1(ii)).

From now on, the term: ‘Pr^{3+}/In small-core SIF’ will be used to denote the two types of small-core SIFs each with 9.51×10^{24} ions m^{-3} (500 ppmw) Pr^{3+} doped Ge-As-In-Se core and undoped Ge-As-In-Se-S cladding, of core-OD as-designed/fiber OD = 20 μm/130 μm or = 40 μm/270 μm, respectively. Additionally, the term ‘unstructured Pr^{3+}/In *intermediate* fiber’ will be used to denote the unstructured fiber composed of 9.51×10^{24} ions m^{-3} (500 ppmw) Pr^{3+}-Ge-As-In-Se and of OD = 230 μm ± 20 μm (see Fig. 1(i)).

2.3. Characterization of bulk glasses and fiber

2.3.1. Glass stability

Powder-XRD was done on samples to test for amorphicity in a Siemens Krystalloflex 810 X-ray diffractometer, with CuKα radiation, in the range 10–70 °2θ, in steps of 0.05 °2θ per 40 s with each XRD pattern collected in ~13 h.

2.3.2. Fiber optical loss

Optical loss of the ‘unstructured Pr^{3+}/In *intermediate* fiber’ (see Fig. 1(i)) was measured in the wavelength range 1–9 μm, using the cut-back method (detailed in Ref. [16]) with an IFS 66/S, Bruker Ft-MIR spectrometer and InGaAs, InSb and MCT detectors; the optical path was not purged. Fig. 2 shows the selected ‘best’ fiber cleaves used in the fiber-loss calculation.

2.3.3. ‘Pr^{3+}/In small-core SIF’ cross sectional geometry

The ‘Pr^{3+}/In small-core SIFs’ (Fig. 1(ii)) were analysed as follows. SIFs were cleaved, and cross sections carbon-coated then imaged and analysed by means of (E(environmental)) SEM-BSE and (E) SEM-EDX (FEG XL30 ESEM) with an Oxford Instruments INCA x-sight Si(Li) detector with ATW2 window.

Near-field, NIR imaging of 55–60 mm long samples was *via* a tunable laser: 1.465–1.575 μm (Agilent; 8164B). 1.465 μm was selected as being off-centre from the 1.45 μm Pr^{3+} absorption [23], with absorption falling sufficiently by 1.465 μm for detection of the guided light. The 1.465 μm light was launched into the ‘Pr^{3+}/In small-core SIFs’ using a tapered silica-fiber, mounted on a XYZ translation stage, with focused spot size 2.5 μm at the chalcogenide