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Praseodymium-doped Ge₂₀In₅Sb₁₀Se₆₅ films based on argon plasma co-sputtering for infrared-luminescent integrated photonic circuits

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Praseodymium-doped $\text{Ge}_{20}\text{In}_5\text{Sb}_{10}\text{Se}_{65}$ films based on argon plasma co-sputtering for infrared- luminescent integrated photonic circuits

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Keywords: amorphous chalcogenides, waveguides, infrared, luminescence, rare earth

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Abstract

In this paper, we report on the infrared luminescence of amorphous praseodymium-doped $\text{Ge}_{20}\text{In}_5\text{Sb}_{10}\text{Se}_{65}$ waveguides, which can be used as infrared sources in photonic integrated circuits on silicon substrates. Amorphous chalcogenide thin films were deposited by radio-frequency magnetron co-sputtering using an Argon plasma whose deposition parameters were optimized for chalcogenide materials. The micro-patterning as ridge waveguides of the chalcogenide co-sputtered films was performed using photolithography and plasma-coupled reactive ion etching techniques. The influence of rare earth concentration within those thin films on their optical properties and rare earth spectroscopic properties was investigated. Using an excitation wavelength of $1.55\ \mu\text{m}$, the mid-infrared luminescence of Pr^{3+} ions from 2.5 to $5.5\ \mu\text{m}$ was clearly demonstrated for this germanium-, antimony-, and indium-based chalcogenide material. A wide range of waveguide widths and doping ratios were tested, assessing the ability of the co-sputtering technique to preserve the luminescence properties of the rare earth ions initially observed in the bulk glass through the thin film deposition and patterning process.

1 - Introduction

Chalcogenide glasses are particularly versatile materials thanks to their rich chemical, electronic, optical, and phase-change properties. These amorphous materials represent a real

1
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3 boon for a whole range of passive and active photonic applications within traditional and
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6 emerging technology platforms ¹. Chalcogenide glasses can be shaped in a variety of ways: in
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9 addition to the basic synthesis generally obtained by conventional melting-quenching, the use
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11
12 of mechanical milling is becoming more widespread ², various fiber-drawing techniques have
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15 also been developed, and the manufacture of amorphous films is essentially carried out via
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17
18 physical vapor deposition (PVD) methods. More recently, the additive manufacturing approach
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21 is also being explored, via the formulation of nanoparticle-based inks and inkjet printing for the
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24 deposition of thin films or 3D printing based on thin glass rods ³.
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30 The applications of chalcogenide glasses in the mid-wave infrared (MWIR) and long-wave
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33 infrared (LWIR) spectral ranges are diverse and numerous given the combination of several
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36 optical properties enabling their use as an infrared optical media. Based on the strong optical
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39 non-linearities of these materials, supercontinuum laser sources spanning up to 13.3 μm ⁴ were
40
41
42 fabricated. Frequency conversion devices from ultraviolet to short-wave infrared (SWIR) based
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45 on As_2S_3 nanowires were also demonstrated ⁵. Chalcogenide materials, known as PCMs (phase
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47
48 change materials), are currently of growing interest in photonics because of their ability to
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51 switch rapidly between amorphous and crystalline phases ⁶.
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4 Considering their optical transparency range, the research and development in the sensor
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7 applications sector was a natural choice representing a passive photonic use of amorphous
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10 chalcogenides. The functional group wavelength domain of chemical species is 2.5-7.5 μm and
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12
13 can be selectively detected using infrared spectroscopy. For instance, the evanescent wave
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16 spectroscopic sensing can be achieved using tapered optical fibers ⁷ or micro-waveguides and
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19 micro-resonators sensing devices ⁸. Coherent light sources for detection of such species as
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22 carbon dioxide, carbon monoxide, NO_x and organic molecules, could provide an accurate
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25 quantification, as the fingerprint of these molecules exhibit high absorption cross-sections in
26
27
28 the infrared spectral range ⁹.

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33 Allowing others potentialities, these chalcogenide glasses could host rare earth (RE) ions ¹⁰.
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36 Nevertheless, only a small amount of RE^{3+} ions of the order of a few hundred ppmw. can be
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39 incorporated into a binary and even ternary chalcogenide glass matrix without causing
40
41
42 crystallization, segregation or clustering. The RE^{3+} ions solubility in these glasses could be
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45 greatly enhanced by the presence of the Ga ions ¹¹, which could also be achieved with the use
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48 of In ions as proposed previously by Aitken et al. ^{11a, 12}. RE-doped chalcogenide glasses could
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51 be drawn into fibers, thus compact and robust fluorescence sources in the MWIR or LWIR
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54 wavelength domains can be provided ¹³. Another application of RE-doped chalcogenide glasses
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3 is the wavelength conversion from the LWIR or MWIR wavelength domain to the SWIR or
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6 visible domain, which was successfully applied to carbon dioxide (4.4 μm) or methane (3.4 μm)
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10 detection with the use of Er^{3+} -doped sulfide fibers ¹⁴. To perform various functions in
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13 telecommunications or optical sensing technologies, and as a complement to the uses of optical
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16 fibers, light source devices are essential in photonics. Thus, photonic platform based on RE
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19 doped chalcogenide films and waveguides have begun to be developed ¹⁰. Erbium luminescence
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21
22 has been demonstrated in waveguide using various deposition techniques such as pulsed laser
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24
25 deposition ^{8d, 15}, thermal co-evaporation ^{8d, 16} or (co)-sputtering ¹⁷. In the recent years,
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27
28 photoluminescence in the MWIR for ions like Er^{3+} , Pr^{3+} or Dy^{3+} have been demonstrated ^{8d, 17a,}
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Our present work focuses on the MWIR luminescence that could be obtained from Pr^{3+} -doped
GeInSbSe ridge waveguides deposited on Si/SiO₂ substrate. We report major improvements
regarding the material composition, the deposition technique and the waveguide fabrication
leading to enhanced MWIR luminescence of the Pr^{3+} ion compared to previous works ^{18c}.

2- Materials and methods

Bulk glasses synthesis and thin films deposition

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3 The Pr³⁺ doped and undoped In₅Ge₂₀Sb₁₀Se₆₅ bulk glasses were synthesized using
4 conventional melting and quenching method. High purity (5N) elements were used to prepare
5
6 the glasses. The selenium was pre-purified by static distillation before the all components (In,
7 Ge, Sb, Se and Pr₂S₃) were weighted and put into a 50 mm diameter silica ampoule. Then, the
8
9 ampoule was sealed and placed in a rocking furnace where the mixture was melted at 950 °C
10 during 2 hours to ensure the homogenization of the melt. The temperature was then decreased
11
12 to 850 °C and consequently to 650 °C, afterwards the ampoule was quenched in water and
13
14 quickly placed in preheated furnace to be annealed at around 10 °C below the glass transition
15
16 temperature. At the end, the silica ampoule was opened and the glass rod was cut and polished
17
18 in order to obtain chalcogenide glass cylinders with thickness of 3.5 mm. The fabricated
19
20 chalcogenide glass cylinders were used as sputtering targets. One of the three targets is doped
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22 with 10,000 ppmw. Pr³⁺ ions, while the other two are undoped to allow tuning of the rare earth
23
24 concentration during the co-deposition process. Another bulk glass, doped at 1000 ppmw. of
25
26 Pr³⁺, was specially fabricated for spectroscopic characterization of praseodymium in In-Ge-Sb-
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28 Se glass matrix. Co-sputtering depositions were performed either on BK7 or single crystalline
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30 silicon substrates. The latter have been previously thermally oxidized resulting to film of SiO₂
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32 with thickness of about 2 μm. The doped target was placed on the cathode 1, whereas the two
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3 undoped ones were placed on cathodes 2 and 3, which enables to control the Pr³⁺ concentration
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7 for the deposited film from 0 to 10000 ppmw. The individual deposition rate for each target
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10 was estimated using different powers (5, 10, 15 and 20 W) under argon atmosphere of 5.10⁻³
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13 mbar. Then, depositions were performed using a combination of different power applied to
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16 individual cathodes to adjust the Pr³⁺ content in the fabricated films. The chemical composition
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19 of the targets and the films was determined via EDS analysis, using a JSM-IT300-LV scanning
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21
22 electron microscope (20 kV) exploiting L emission lines of In, Ge, Sb and Se, with a
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25 measurement uncertainty of ±1 at. percent. The DSC measurements of bulk glasses were done
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28 using a temperature ramp of 10 °C.min⁻¹.
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32 33 **Thin film characterization**

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37 The Raman spectrometer device is a LabRam μ-Raman HR Evo from Horiba Scientific, with
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40 a focal length of 800 mm, an excitation wavelength of 785 nm and coupled with a x100
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43 microscope objective. The Raman spectra were recorded for films deposited on BK7 substrates
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46 to avoid background Raman signal from the Si substrates. The thermal population effects were
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49 accounted and treated using the reduced Raman intensity following Shuker and Gammon's
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52 work ¹⁹.
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3 Spectroscopic ellipsometry was employed to determine films thickness and optical functions
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6 in the UV-VIS-NIR-MIR region using two variable-angle spectroscopic ellipsometers (VASE
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10 and IR-VASE, both J.A. Woollam Co.): first one with a rotating analyzer operating in the UV-
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13 VIS-NIR range (300-2300 nm) and second one with a rotating compensator covering
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16 wavelengths between 1.7 and 30 μm . The Cody-Lorentz and Sellmeier models were used to
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19 analyze spectroscopic ellipsometry data in UV-VIS-NIR and MIR region respectively. Bulk
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22 refractive indexes were measured in the SWIR using a prism-coupling technique apparatus
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25 (Metricon 2010/M). For the AFM (Ntegra2-NT-MTD), experiments, the tip model was HA-
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28 NC, the scanning rate was set from 0.5 to 0.8 Hz, and scans were made for two different square
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31 sizes (5 and 2 μm^2). The roughness was estimated for the two smallest square sizes. On 400-
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34 nm thick samples deposited on Si/SiO₂ substrates, the measured RMS roughness was measured
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37 below 0.25 nm, which shows that the deposited thin films are pretty smooth. To determine the
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40 band-gap energy calculation in order to respect the condition of Tauc's law application,
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43 characterizations were also performed on 400-nm thick films deposited on BK7 substrates at
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46 15 W and under Ar pressure of 5.10^{-3} mbar for each individual target.
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52 53 **Waveguides etching and fabrication** 54 55 56 57 58 59 60

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3 Fabrication of ridge waveguides of different widths (ranging from 1.5 to 10 μm) were
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6 performed using a classical i-line photolithographic process followed by a dry etching
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9 procedure. A MJB4 Suss Microtech mask aligner was used to expose the positive S1805
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12 photoresist (Microposit) through a Cr mask. An inductively coupled plasma-reactive ion
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14 etching (ICP-RIE) process (Corial 200IL) was then used with CHF_3 gas to transfer the pattern
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17 to the doped selenide film.
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23 **Optical setups: benches descriptions**

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26 The transmission spectra were determined in the visible domain using a Perkin Elmer Lambda
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29 1050 spectrophotometer, while the MWIR $\text{Pr}^{3+} \ ^3\text{H}_4 \rightarrow \ ^3\text{H}_5$ absorption was measured using a
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31
32 Bruker Tensor 37 FTIR spectrophotometer. For the bulk glass luminescence spectra acquisition,
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35 a conventional fluorescence setup composed of a monochromator associated with a lock-in
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38 amplifier was used. The infrared detector was a nitrogen-cooled InAsSb chip (Hamamatsu).
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41 The pumping source was a Q-Photonics QSM-1550-3 laser diode, modulated at the frequency
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44 of 23 Hz. For lifetime measurements, the laser diode controller was operated in pulsed regime,
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48 which enables the control of the pulse width and period. Fluorescence decays were recorded
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51 using a Textronix TDS 3032 oscilloscope. Pulse width and period were of 30 ms and 150 ms
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3 respectively. Absorption and lifetimes experiments were conducted on bulk samples. Judd-
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6 Ofelt calculations were performed following a standard method ¹².
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10 Guided fluorescence in co-propagative configuration was recorded at room temperature on a
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12 dedicated bench equipped with sub-micron precision flexure stages. The waveguides were
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14 cleaved perpendicularly to the channel's orientation, a length of 5 mm for all samples was
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16 selected. A 50 mW continuous ASE (Amplified Spontaneous Emission) source emitting around
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18 1.55 μm was injected into the waveguide using custom made micro-lensed fibers (mode field
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20 diameter of 2.4 μm) to reduce coupling losses.
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30 The fluorescence at waveguide output was collected using a ZnSe aspheric lens (Thorlabs),
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32 and then passed to a monochromator (Horiba iHR320). For the SWIR and MWIR spectrum
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34 acquisition, a 4 μm -blazed grating (150 lines/mm) was used. The transmitted pump and second-
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36 order luminescence was removed using either long-pass edge filters with cut-off wavelengths
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38 of 1.9 or 3.5 μm . The detector was a nitrogen-cooled InSb chip (Teledyne Judson
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40 Technologies), and electrical signal recovery was done by a SR830 lock-in amplifier (Stanford
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42 Research Systems).
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52 53 **3- Results and discussions**

54 55 56 57 **Glasses and thin films properties** 58 59 60

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4 The glass transition temperature (T_g) was found to be around 261 ± 2 and 255 ± 2 °C °C for
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6
7 the Pr^{3+} (10000 ppmw.) doped and undoped $\text{In}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$ bulk glass targets, respectively.
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10 The density is around 4.69 ± 0.01 and 4.67 ± 0.01 $\text{g}\cdot\text{cm}^{-3}$ for doped and undoped glass,
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12
13 respectively. The T_g values are close between the different targets, considering the uncertainty
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15
16 of the measurements, with a slight increase with rare earth doping, and even closer considering
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19 density.
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24 After the determination of individual deposition rates as a function of the cathode power, a
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27 linear combination of these powers allowed the deposition of typically 1 μm thick films, with a
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30 Pr^{3+} doping level tuned from 0 to 10,000 ppmw. The estimated Pr^{3+} concentration in the
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32
33 deposited films, ranging from 1300 ppmw. to 10,000 ppmw, as calculated from single cathode
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35
36 deposition rates, is reported in Table 1. Targets and films compositions from an EDS analysis
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38
39 are reported in Table 1. For the thin films, the chemical analysis was performed on a piece of
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42 sample taken just aside of the etched part of the thin film used for the luminescence experiments
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45 on Pr^{3+} : In-Ge-Sb-Se waveguides.
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Bulk glass target	RE [ppmw.]	In	Ge	Sb	Se
Cathode 1	10,000	4	19	10	67
Cathode 2	undoped	5	22	8	65

Cathode 3	undoped	6	21	8	65					
Thin film deposition	RE [ppmw.]	In	Ge	Sb	Se	Powers [W]			Thickness [nm]	Dep. rate [nm/min]
						C1	C2	C3		
1	2500		22	7	66	8	15	15	1040	10.4
2	2500	4	22	7	67	9	10	10	1050	6.2
3	4100	5	20	8	68	15	10	10	1140	8.4
4	7500	4	20	8	68	20	5	5	1000	6.9
5	10,000	4	18	10	68	20	0	0	1030	5.4

Table 1: Co-sputtering parameters used for the deposition of Pr³⁺: In-Ge-Sb-Se thin films, EDS analysis of the bulk targets and the co-sputtered thin films, thickness (± 5 nm) and deposition rate of the co-sputtered films.

The undoped target composition shows a deficit of antimony and excess of Ge of about 1-2% with respect to the doped target, whereas the latter has an excess of selenium of 2% compared to the desired nominal composition, which was Ge₂₀In₅Sb₁₀Se₆₅. The composition of the deposited thin films depends on both, the composition of the targets used and the deposition parameters. It should also be borne in mind that the determination of the composition in multicomponent films remains delicate and even more so in the case of a thin film of 1 μ m. The analysis of the chemical composition of the thin films shows an overall slight increase in Se content (+ 1 to 3%) to the detriment of Sb (- 2 to 3%, except for the 10,000 ppmw.). The germanium gradually goes from an excess (+2%) to a deficit (-2%) according to the concentration of the Pr³⁺ ions increasing by applying more power on target C3. This change in

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3 germanium concentration fully reflects the influence of target composition. With regard to
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7 indium, its concentration remains stable in accordance with the compositions of the targets and
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10 within the limits of the measurement it corresponds well to the desired concentration with
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13 perhaps a slight deficit (-1%). The 1300 and 2500 ppmw. thin films are very close in
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16 composition to undoped targets. The antimony level corresponds to the measurement
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18
19 uncertainty due to the composition of the undoped targets. The influence of the Pr³⁺ doped
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21
22 target which has a lower concentration of germanium and a higher concentration of antimony
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24
25 can be felt on the thin film composition from the film at 4100 ppmw. Finally, the composition
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28 of the film containing 10,000 ppmw. of Pr³⁺ is very close to the C1 target used for its deposition.
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31 We note that all the thin films present slight excess of selenium. The pressure of 5.10⁻³ mbar
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34 was determined from previous experiments, which made it possible to obtain thin films with
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37 high density, low roughness and IR luminescence in the near and medium infrared. On the other
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40 hand, selenium have higher sputtering efficiencies and higher volatility than Ge and Sb, the
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43 selenium concentration in sputtered thin films tended to be lower than that of the target for low
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46 Ar pressure even at room temperature ¹⁹⁻²⁰. The expected deficit in selenium of the Ge-In-Sb-
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49 Se sputtered thin films is ultimately compensated here with the use of targets richer in selenium
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57 than a stoichiometric bulk target.
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Raman scattering spectroscopy

The normalized reduced intensity Raman spectra recorded for fabricated thin films are reported in Figure 1(a). The Raman spectra were also measured for thin films deposited from each individual target, as depicted in Figure 1(c). All Raman spectra were normalized with respect to the 198 cm^{-1} peak attributed to the Ge-Se bonds in corner-sharing $[\text{GeSe}_4]$ tetrahedra. This normalization was arbitrarily done in order to facilitate a comparison between the intensity of the various bands present in the Raman spectra. The 305 cm^{-1} contribution that is only visible in the deposited films spectra is due to the oxidized Si substrate (Figure 1(a)). Specific contribution from the vibration modes associated to In-Se bonds (as described for InSe evaporated thin films ²¹) is not clearly identified since there is strong overlap with Ge-Se bonds modes peaking at around 200 cm^{-1} .

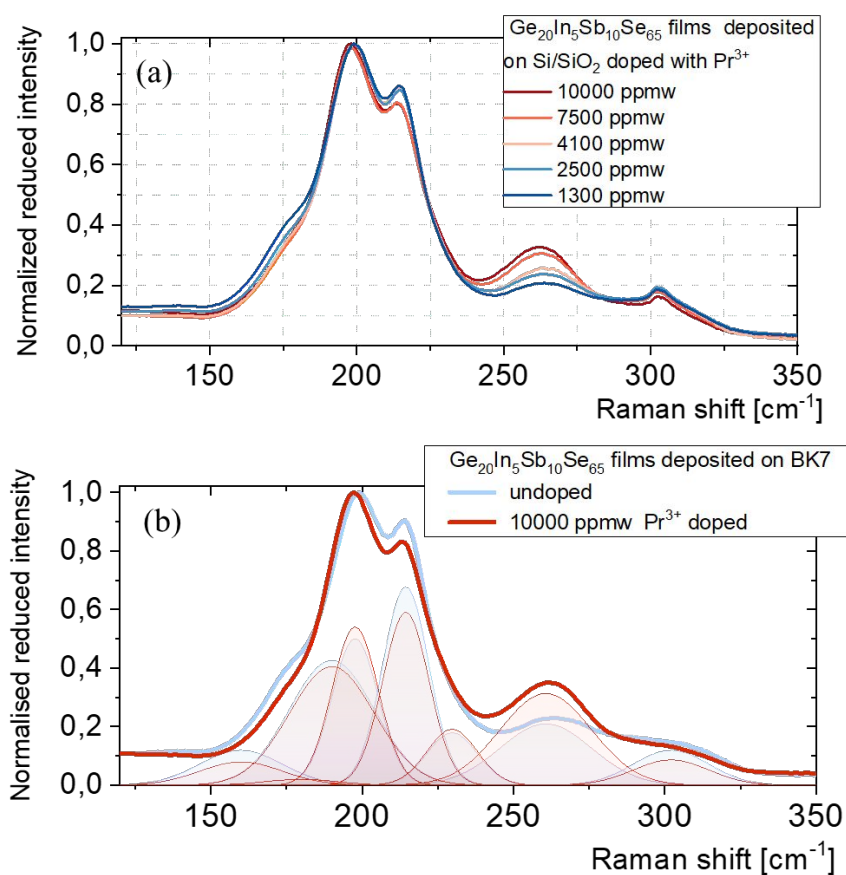


Figure 1: (a) Normalized reduced Raman spectra of the Pr³⁺: Ge₂₀In₅Sb₁₀Se₆₅ thin films for various Pr³⁺ concentrations deposited on Si substrates; (b) Pr³⁺ doped and undoped Ge₂₀In₅Sb₁₀Se₆₅ films deposited from single undoped and 10,000 ppmw. doped cathodes on BK7 substrates.

The 215 cm⁻¹ mode, attributed to the edge-sharing [GeSe₄]²⁰, is showing some relative decrease with the doping rate, in line with the increasing use of the 10,000 ppmw. target with a lower intensity of this mode. This is in agreement with what was observed for the 265 cm⁻¹ vibration of the Se_n chains, which also follows the same trend associated with the use of the

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3 10,000 ppmw. target. The increase in the relative value observed is generally attributed to an
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6 increase in Se content ²⁰. It is confirmed by the EDS measurements with the Se rate going from
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10 65 to 67% for the doped target and sputtered thin films. Moreover, Ge-Sb bonds intensity
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13 variations could be observed at 165 cm⁻¹ related to the use of the different targets. All
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16 intermediates situations are to be found in the Raman spectra of deposited films (Figure 1(b)),
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19 with a gradual increase of the 265 cm⁻¹ and decrease of the 215 cm⁻¹ and 170 cm⁻¹ bands with
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22 the doping rate. This is not due to the rare earth doping itself, but to the fact that the proportion
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25 of material originating from the rare earth-doped target is much greater in the deposited film
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28 when the power applied to this target is increased, compared with undoped targets. Thus, the
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31 envelope of the film's Raman spectrum should tend towards that of the rare earth-doped target
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34 with increasing rare earth concentration, as observed experimentally.
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40 **Optical properties of the sputtered thin films**

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43 From the transmission measurements, the band-gap energy $E_g^{opt}(\pm 0.02 \text{ eV})$ is derived from
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46 Tauc plots ²². E_g^{opt} was estimated to be around 1.85 and 1.81 eV for undoped thin films and thin
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49 film doped with 10,000 ppmw. of Pr³⁺, respectively. The E_g^{opt} discrepancies are mainly
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52 reflecting the composition variations of these two films ⁸. The dispersion curves of the refractive
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55 index obtained from ellipsometric measurements are shown in Figure 2.
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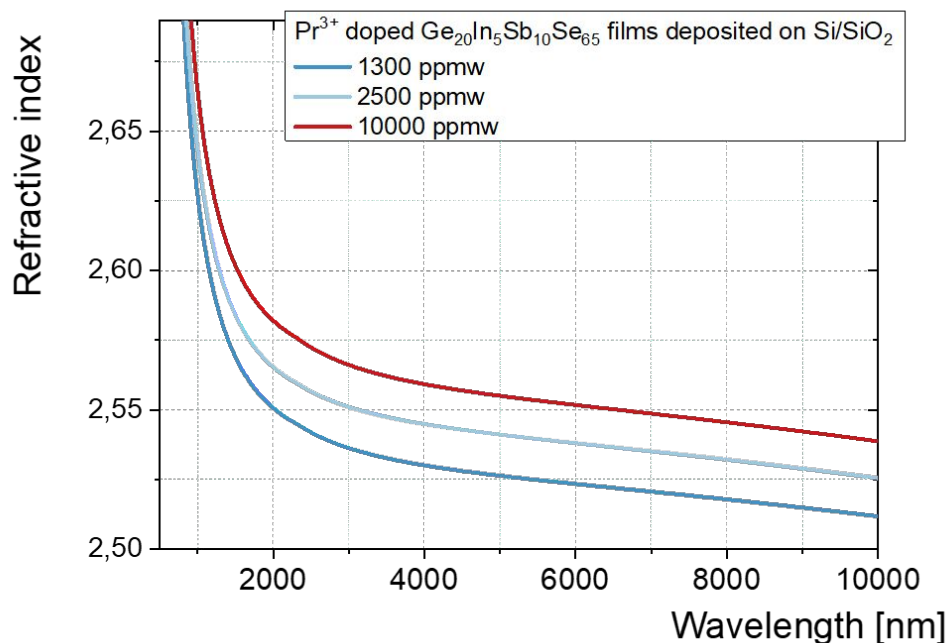


Figure 2: Refractive index spectral dependences of Pr^{3+} doped GeInSbSe thin films with different doping level (1300, 2500 and 10,000 ppmw).

For the 10,000 ppmw. doped film, refractive indexes at the representative wavelengths 1.55 (pump absorption), 2.5 (SWIR emission) and 4.5 μm (MWIR emission) are equal to 2.60, 2.57 and 2.56 respectively, in close agreement with the values measured for $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$ thin films within the presence of Ga instead of In for the 10,000 ppmw. doped film (2.61, 2.58 and 2.57)^{18b}. Usual behavior can be seen, with the refractive index increasing with the addition of praseodymium for atomic weight reason. The chemical composition of the films also slightly varies and will have an impact on the refractive index of the thin films. The progressive increase of antimony to the detriment of germanium with a larger content of selenium when the Pr^{3+}

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3 concentration increases will impact the refractive index of the thin films with an expected
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6 increase. Even if these changes remain relatively controlled within a range of only a few
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9 percent, they alone can explain the observed trend. All these values are comparable to those
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12 measured on bulk glass targets, the 1.55 μm refractive indexes are of 2.60 and 2.61 for the
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15 undoped and doped bulk glass targets respectively.
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20 **Spectroscopic properties**

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23 Spectroscopic properties of Pr^{3+} doped GeInSbSe glass were investigated using a 1000 ppmw.
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26 doping level, which is satisfactory large to measure the absorption spectrum with a good signal
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29 to noise ratio over a few millimeters thick bulk glass sample. Furthermore, the doping level is
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32 low enough to limit the dipole interactions, which could lead to luminescence quenching. This
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35 enables to determine the quantum efficiency ($\eta = \tau_{\text{F}} / \tau_{\text{R}}$) for each manifold. The radiative
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38 lifetime (τ_{R}) is deduced from Judd-Ofelt calculations ²³.
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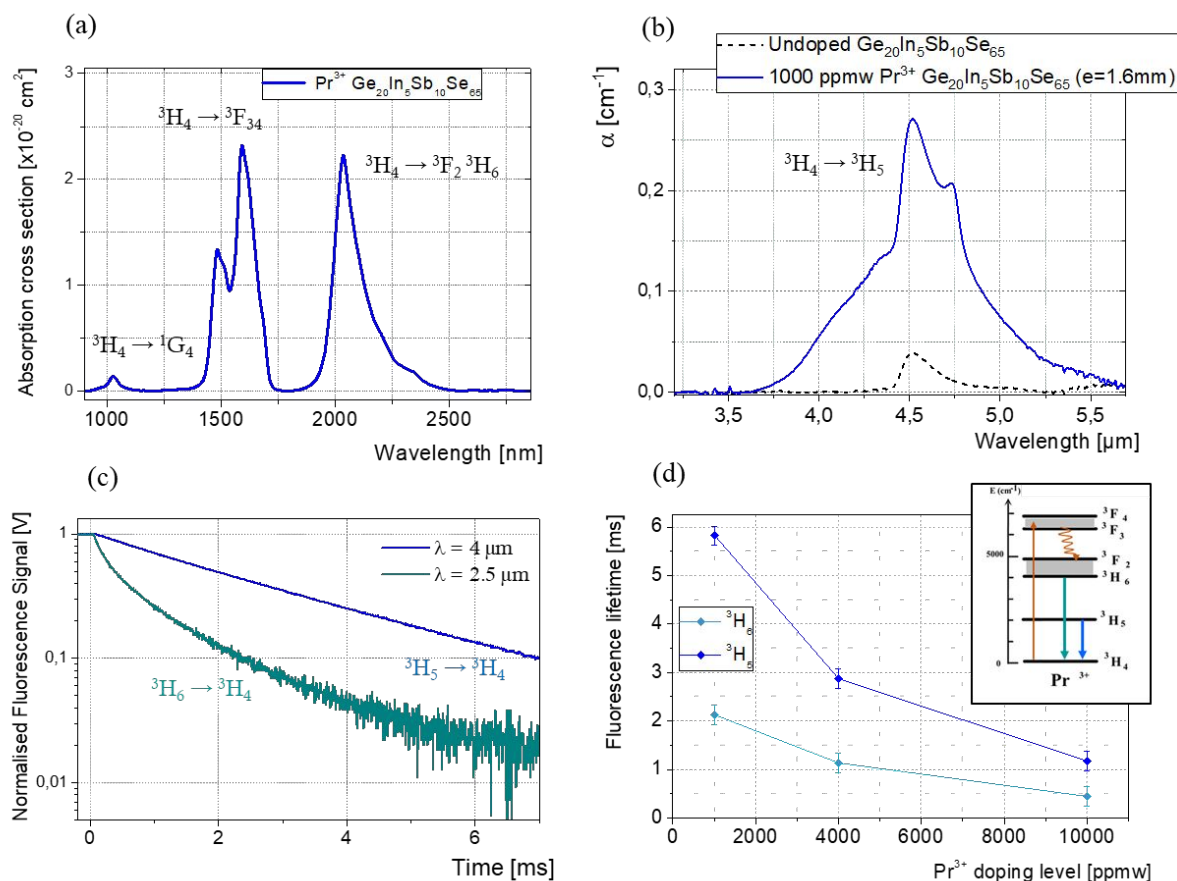


Figure 3. (a) Absorption cross section calculated from the 1000 ppmw. Pr³⁺ GeInSbSe in the SWIR and (b) absorption coefficient in the MWIR domains; (c) fluorescence decays recorded in the SWIR and MWIR for the 1000 ppmw. doped glasses; (d) Fluorescence lifetime for the Pr³⁺ 3H_6 and 3H_5 manifolds as a function of Pr³⁺ concentration in bulk glasses and Pr³⁺ simplified energy diagram (inset).

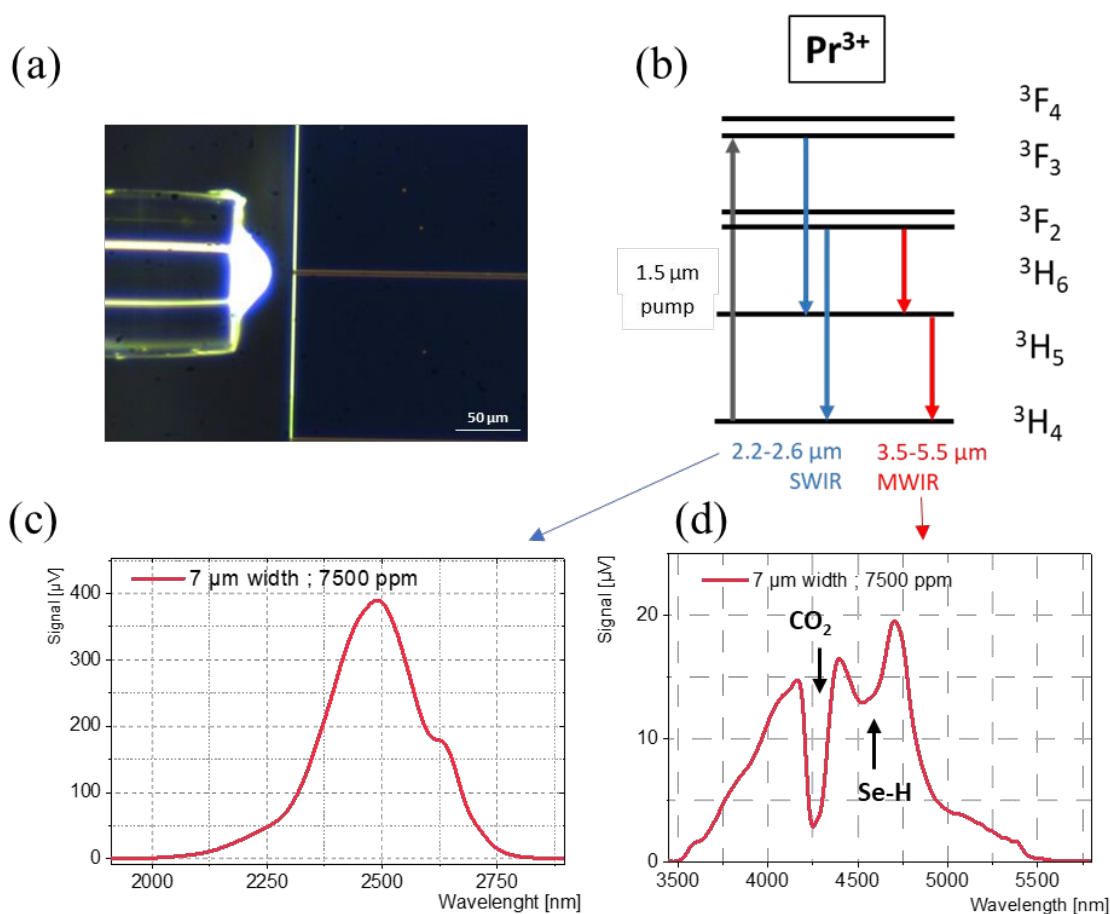
Figures 3(a) report the absorption cross section of Pr³⁺ ion obtained for a 1000 ppmw. doped Pr³⁺ GeInSbSe glass, showing the electron transitions used for the Judd-Ofelt parameters calculation. The corresponding absorption cross-sections were calculated from baseline

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3 corrected transmission spectra. The 1G_4 GSA (Ground State Absorption) is clearly identified,
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6 while the $^3F_3, ^3F_4$ and $^3F_2, ^3H_6$ GSAs are overlapped, which requires a spectrum deconvolution.
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10 The Se-H absorption band (observed for undoped GeInSbSe glass as shown in Figure 3b) was
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13 subtracted from the 3.5-5 μm absorption band for the cross section calculation of the transition.
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16 The calculated Judd-Ofelt parameters $\Omega_{2,4,6}$ are (2.3; 4.7; 5.12). 10^{-20} cm^2 , leading to
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19 calculated radiative lifetimes for the $^3F_4, ^3H_6$ and the 3H_5 manifolds of 316 μs , 6.2 and 16.7 ms
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22 respectively, which are higher than values reported in the literature ²⁴. Computed radiative
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25 lifetimes were compared to the experimental data. As one can see in Figure 3(c), a combination
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28 of fast and slow exponential decays is necessary to describe the 3H_6 decay ²⁵. For the 1000
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31 ppmw. doped bulk glass, fluorescence lifetimes of 185 μs and 2.12 ms (± 0.2 ms) were found
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34 for the 3H_6 , while the 3H_5 shows a single exponential decay with a 5.82 ms time constant. When
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37 compared to $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$ chalcogenide glasses, the lifetimes for the same doping levels are
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40 higher in the GeInSbSe glass ²⁶. For the 3H_5 manifold lifetime, the value for GeInSbSe glass is
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43 lower than the 11.5 ms obtained for 500 ppmw. doped Pr^{3+} Ge-As-Ga-Se glasses ²⁴. Finally,
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46 fluorescence lifetimes for the 3H_6 and 3H_5 manifolds were measured for several doping levels
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49 within the GeInSbSe glass (Figure 3d), giving an idea of luminescence quenching effect
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53 increasing with the Pr^{3+} concentration.
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Consequently, emission properties were investigated with the prepared set of waveguides. In Figure 4(a), the typical injection scenario for any waveguide is shown. The lensed tip of the fiber is bright, and its working distance from the input face is a few tens of micrometers. With 1.55 μm pump beam, the expected fluorescence transitions from Pr^{3+} infrared manifolds are described in Figure 4(b). Moreover, the ${}^3\text{H}_5 \rightarrow {}^3\text{H}_4$ transition of Pr^{3+} ion, which is mainly contributing to the MWIR fluorescence (${}^3\text{H}_6 \rightarrow {}^3\text{H}_5$ also but with a lower probability), is a transition ending on the ground state ${}^3\text{H}_4$. This particularity gives rise to a strong reabsorption along the fluorescence optical path ^{18b}.



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4 Figure 4. (a) optical microscope observation of the in-coupling region showing the lensed fiber
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7 and a 3- μm wide channel waveguide; (b) Pr^{3+} simplified energy diagram for the SWIR and
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10 MWIR emissions; (c) SWIR and (d) MWIR luminescence of a 7 μm wide 7500 ppmw. Pr^{3+}
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13 doped GeInSbSe ridge waveguide.
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18 The examples shown in Figure 4(c,d) are typical of the fluorescence spectra that have been
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21 recorded for large waveguides at any doping level. For the 7- μm -wide waveguide of 7500
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24 ppmw. Pr^{3+} doped film, both SWIR and MWIR emissions are recorded with good signal to
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27 noise ratio (integration time 1 s). The guided fluorescence is mainly affected along the channel
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30 by the reabsorption of impurities like Se-H (4.5 μm) in agreement with published results of Ga-
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33 containing waveguides ^{18b}. The carbon dioxide infrared absorption peaking at 4.3 μm occurs
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36 along the free space propagation of the infrared fluorescence from the waveguide output facet
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39 to the detector entrance. Since the large waveguides (wider than 3 μm) give good signal to noise
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42 ratio in the SWIR and MWIR domains, luminescence from waveguides of smaller dimensions
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45 displaying singlemode ($w < 2.5\mu\text{m}$) or few-order modes propagation at MWIR wavelengths
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48 could also be investigated. The results presented below are the averaged spectra obtained from
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51 the 2.0, 2.5 and 3.0 μm channels, which corresponds to reduced amount of propagating modes
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in every case. For these narrow waveguides, the average signal of SWIR and MWIR luminescence spectra for all Pr³⁺ doping levels are presented in Figure 5(a,b).

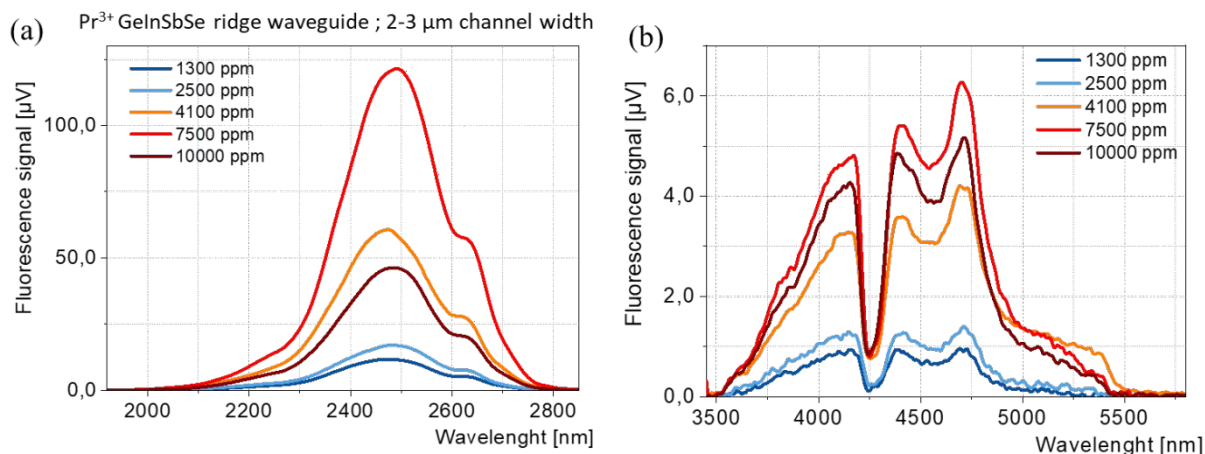
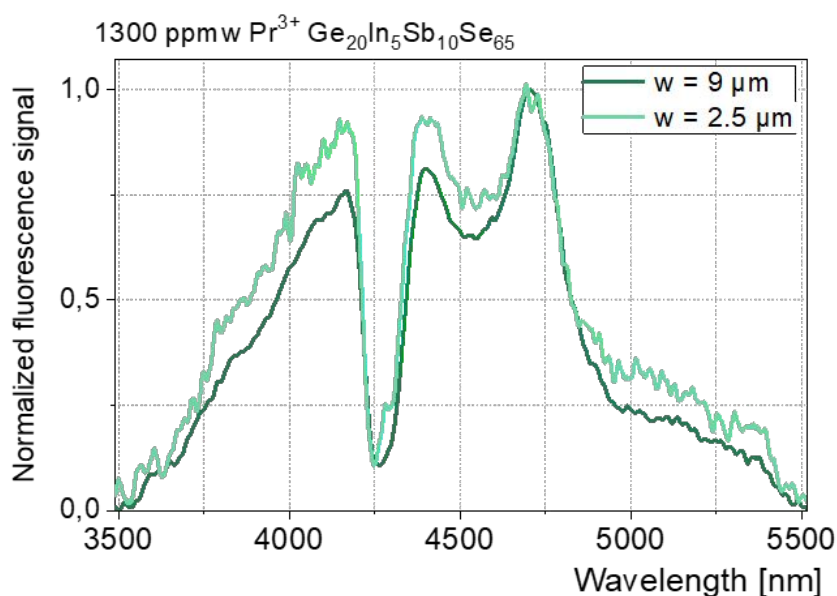


Figure 5. Averaged (a) SWIR and (b) MWIR emissions measured for Pr³⁺ doped GeInSbSe ridge waveguides widths of 2.0, 2.5 and 3.0 μm.

No guided luminescence was recorded for waveguides widths smaller than 1.5 μm, confirming mode simulations showing that the cut-off width at MWIR wavelengths is below 1.5 μm^{18b}. The 1.5 μm channel waveguide is the inferior width limit for MWIR modes propagations, so injection in smaller channels was not performed. In previous work using the same experimental setup for characterization of Pr³⁺ Ga-Ge-Sb-Se ridge waveguides^{18b}, raw signal intensities were lower than those recorded here, even with the use of 8 μm channel width at the same conditions (pumping power and optical setup).

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4 A 7500 ppmw. doped waveguide was found to be the most efficient infrared luminescence
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7 emitter fabricated in this work. The raw intensities, when compared, showed that 2.5 μm wide
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10 channel generates at least 3 times more luminescence signal in both wavelength domains than
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13 the best 8 μm wide Pr^{3+} Ga-Ge-Sb-Se channel waveguide^{18b}. For such Pr^{3+} -doped Ge-In-Sb-Se
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16 waveguides MWIR waveguide luminescence was obtained at any doping level, but the case of
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20 1300 ppmw. doped 1.5 μm width waveguide the signal to noise ratio must be discussed.
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Figure 6. MWIR luminescence from 1300 ppmw. doped Pr^{3+} GeInSbSe single mode waveguides signal compared to multimode waveguides.

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Figure 6 shows the MWIR normalized fluorescence spectra obtained for single and multimode waveguides for the 1300 ppmw. sample. The emission spectrum of single mode waveguides is

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4 noisy, but still the shape of the Pr^{3+} MWIR emission matches the emission shape of the wider
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7 waveguide.
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11 For these waveguides dimensions, the single mode operation in the MWIR was already
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14 demonstrated, and the same single mode regime could be obtained using a sulfide based buffer
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17 deposited on silicon or oxidized silicon wafers, as calculated for a $1 \times 1.5 \mu\text{m}^2$ doped channel
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20 deposited on a GeSbS confinement film ^{18b}.
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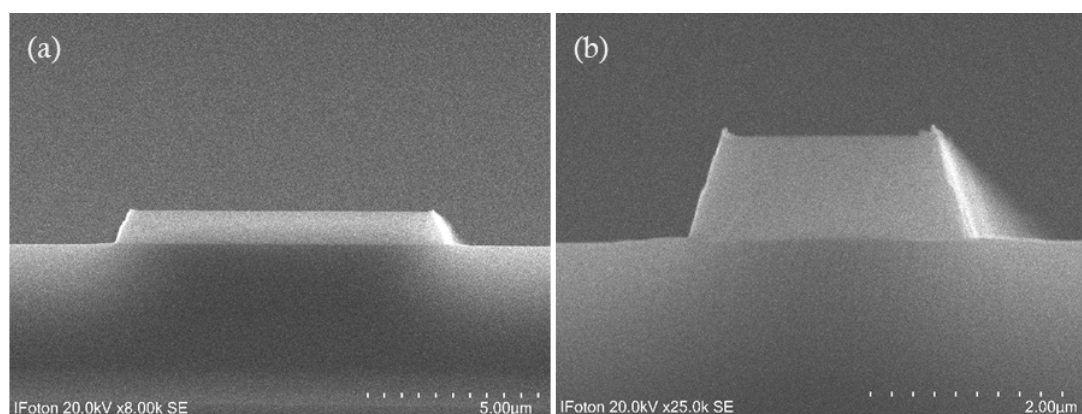


Figure 7. SEM images of 7500 ppmw. Pr^{3+} : GeInSbSe waveguide of (a) 9 μm and (b) 2 μm width.

When compared to the previous results obtained with Pr^{3+} -doped Ga-Ge-Sb-Se waveguides, the fluorescence intensities are in all comparable cases (dimensions, doping) higher using the In-Ge-Sb-Se glass to host the Pr^{3+} ions, which was also the conclusion of another study focused on the Pr^{3+} luminescence in chalcogenide bulk glasses ²⁶. Nevertheless, this is also the result of

more efficient etching process applied to In-Ge-Sb-Se thin films (Figure 7), which gives higher sharpness on the channels top surface. An optimization of the etching process is, however, currently in progress in order to further optimize etching conditions and achieve better sidewall verticality.

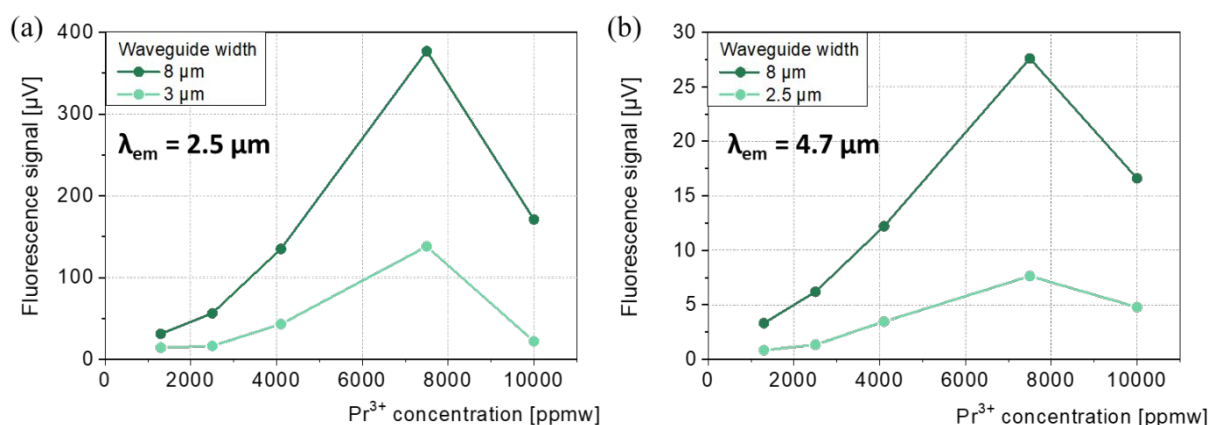


Figure 8. Maximum emission intensities recorded in the (a) SWIR (2.5 μm) and (b) in the MWIR (4.7 μm), for the 8 μm and 2.5 μm wide channels, as a function of the Pr^{3+} concentration in the GeInSbSe waveguide.

Figure 8 reports the maximum emission intensities recorded in the SWIR (2.5 μm) and in the MWIR (4.7 μm), for the 8 μm and 2.5 μm wide channels, as a function of the Pr^{3+} concentration in the waveguide. The trend is reproducible, and the 7500 ppmw. doped sample gives the highest emission in any configuration. This doping level is common for Pr^{3+} doped laser materials, in which typically the Pr^{3+} concentration is about 5000-7000 ppmw. to have efficient

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3 amplification. In agreement, Figure 8 indicates that 6000-8000 ppmw. Pr³⁺ concentration
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6 window would give efficient MWIR emitting films of GeInSbSe material.
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10 Furthermore, infrared lasers could be obtained using 500 ppmw. doped Pr³⁺ Ga-Ge-As-Se
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12 fibers ²⁷. A limitation was the doping level of praseodymium, which could barely exceed 1000
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14 ppmw. without crystallization during the fiber drawing, even following an incident-free
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16 preform elaboration with higher doping rates. The co-sputtering technique permits the
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18 fabrication of highly doped waveguides, with a dopant concentration 10 times higher than its
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20 fiber counterpart, which might increase the capability of fabricated waveguides for laser
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22 operation.
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33 **4- Conclusion**

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36 The Pr³⁺ Ge₂₀In₅Sb₁₀Se₆₅ waveguides deposited by the co-sputtering technique proved to be
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38 an efficient medium for MWIR luminescence generation from a telecom band pumping at 1.55
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40 μm. The co-sputtering technique permits the elaboration of films with a thickness of about 1
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42 μm, with a Pr³⁺ concentration scale from 1300 to 10,000 ppmw, with a maximum drift in the
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44 film composition of 3 at.% with respect to the target composition. The measured film refractive
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46 index is in agreement with its bulk counterpart. These doped films are emitting broad SWIR
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48 and MWIR luminescence bands that could be used for chemical sensing purposes for a large
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3 span of Pr^{3+} concentrations and waveguide geometry. The 2.5 μm wide channels on a 7500
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7 ppmw. doped film gave a clear signal to noise ratio in both SWIR and MWIR domains (single
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10 mode operation), emphasizing the potential of such an active device to be further embedded as
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13 a component for telecommunication or sensing applications.
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40 **References**

- 41
42
43
44 1. Gholipour, B.; Elliott, S. R.; Müller, M. J.; Wuttig, M.; Hewak, D. W.; Hayden, B. E.;
45 Li, Y.; Jo, S. S.; Jaramillo, R.; Simpson, R. E.; Tominaga, J.; Cui, Y.; Mandal, A.; Eggleton, B.
46 J.; Rochette, M.; Rezaei, M.; Alamgir, I.; Shamim, H. M.; Kormokar, R.; Anjum, A.; Zeweldi,
47 G. T.; Karnik, T. S.; Hu, J.; Kasap, S. O.; Belev, G.; Reznik, A., Roadmap on chalcogenide
48 photonics. *Journal of Physics: Photonics* **2023**, *5*(1), 012501.
49
50
51 2. Denoue, K.; Le%Coq, D.; Calers, C.; Gautier, A.; Verger, L.; Calvez, L., New synthesis
52 route for glasses and glass-ceramics in the $\text{Ga}_2\text{S}_3\text{Na}_2\text{S}$ binary system. *Materials Research*
53 *Bulletin* **2021**, *142*, 111423.
54
55
56 3. (a) Carcreff, J.; Chevire, F.; Galdo, E.; Lebullenger, R.; Gautier, A.; Adam, J. L.; Coq,
57 D. L.; Brilland, L.; Chahal, R.; Renversez, G.; Troles, J., Mid-infrared hollow core fiber drawn
58
59
60

- 1
2
3
4 from a 3D printed chalcogenide glass preform. *Opt. Mater. Express* **2021**, *11* (1), 198-209; (b)
5 Ahmed Simon, A.; Badamchi, B.; Subbaraman, H.; Sakaguchi, Y.; Jones, L.; Kunold, H.; J.
6 van Rooyen, I.; Mitkova, M., Introduction of Chalcogenide Glasses to Additive Manufacturing:
7 Nanoparticle Ink Formulation, Inkjet Printing, and Phase Change Devices Fabrication.
8 *Scientific Reports* **2021**, *11* (1), 14311.
9
10
11 4. Venck, S.; St-Hilaire, F.; Brilland, L.; Ghosh, A. N.; Chahal, R.; Caillaud, C.;
12 Meneghetti, M.; Troles, J.; Joulain, F.; Cozic, S.; Poulain, S.; Huss, G.; Rochette, M.; Dudley,
13 J.; Sylvestre, T. In *2-10 μm mid-infrared supercontinuum generation in cascaded optical fibers:
14 experiment and modelling*, Proc.SPIE, 2020; p 1126409.
15
16 5. Gao, J.; Vincenti, M. A.; Frantz, J.; Clabeau, A.; Qiao, X.; Feng, L.; Scalora, M.;
17 Litchinitser, N. M., Near-infrared to ultra-violet frequency conversion in chalcogenide
18 metasurfaces. *Nature Communications* **2021**, *12* (1), 5833.
19
20 6. (a) Ríos, C.; Du, Q.; Zhang, Y.; Popescu, C.-C.; Shalaginov, M. Y.; Miller, P.; Roberts,
21 C.; Kang, M.; Richardson, K. A.; Gu, T.; Vitale, S. A.; Hu, J., Ultra-compact nonvolatile phase
22 shifter based on electrically reprogrammable transparent phase change materials. *PhotonIX*
23 **2022**, *3* (1), 26; (b) Zhang, Y.; Chou, J. B.; Li, J.; Li, H.; Du, Q.; Yadav, A.; Zhou, S.;
24 Shalaginov, M. Y.; Fang, Z.; Zhong, H.; Roberts, C.; Robinson, P.; Bohlin, B.; Ríos, C.; Lin,
25 H.; Kang, M.; Gu, T.; Warner, J.; Liberman, V.; Richardson, K.; Hu, J., Broadband transparent
26 optical phase change materials for high-performance nonvolatile photonics. *Nature*
27 *Communications* **2019**, *10* (1), 4279.
28
29 7. Cui, S.; Boussard-Plédel, C.; Lucas, J.; Bureau, B., Te-based glass fiber for far-infrared
30 biochemical sensing up to 16 μm. *Opt. Express* **2014**, *22* (18), 21253-21262.
31
32 8. (a) Pi, M.; Zheng, C.; Ji, J.; Zhao, H.; Peng, Z.; Lang, J.; Liang, L.; Zhang, Y.; Wang,
33 Y.; Tittel, F. K., Surface-Enhanced Infrared Absorption Spectroscopic Chalcogenide
34 Waveguide Sensor Using a Silver Island Film. *ACS Applied Materials & Interfaces* **2021**, *13*
35 (27), 32555-32563; (b) Pan, J.; Li, Q.; Feng, Y.; Zhong, R.; Fu, Z.; Yang, S.; Sun, W.; Zhang,
36 B.; Sui, Q.; Chen, J.; Shen, Y.; Li, Z., Parallel interrogation of the chalcogenide-based micro-
37 ring sensor array for photoacoustic tomography. *Nature Communications* **2023**, *14* (1), 3250;
38
39 (c) Baudet, E.; Gutierrez-Arroyo, A.; Němec, P.; Bodiou, L.; Lemaitre, J.; De Sagazan, O.;
40 Lhermitte, H.; Rinnert, E.; Michel, K.; Bureau, B.; Charrier, J.; Nazabal, V., Selenide sputtered
41 films development for MIR environmental sensor. *Opt. Mater. Express* **2016**, *6* (8), 2616-2627;
42
43 (d) Yan, K.; Vu, K.; Wang, R.; Madden, S., Greater than 50% inversion in Erbium doped
44 Chalcogenide waveguides. *Opt. Express* **2016**, *24* (20), 23304-23313.
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3
4 9. Hänsel, A.; Heck, M. J. R., Opportunities for photonic integrated circuits in optical gas
5 sensors. *Journal of Physics: Photonics* **2020**, *2*(1), 012002.
- 6
7 10. Nazabal, V.; Adam, J.-L., (INVITED)Infrared luminescence of chalcogenide glasses
8 doped with rare earth ions and their potential applications. *Optical Materials: X* **2022**, *15*,
9 100168.
- 10
11 11. (a) Aitken, B. G.; Ponader, C. W.; Quimby, R. S., Clustering of rare earths in GeAs
12 sulfide glass. *Comptes Rendus Chimie* **2002**, *5*(12), 865-872; (b) Kim, J. K.; Kyou Jin, B.;
13 Chung, W. J.; Park, B. J.; Heo, J.; Choi, Y. G., Influence of the Ga addition on optical properties
14 of Pr in GeSbSe glasses. *Journal of Physics and Chemistry of Solids* **2011**, *72*(11), 1386-1389.
- 15
16 12. P. Nemeč, M. B., M. Frumar, Spectroscopic properties of Pr³⁺ ion in Ge-In-S
17 chalcogenide glasses. *Journal of Optoelectronics and Advanced Materials* **2005**, *7*(5), 2247.
- 18
19 13. (a) Sojka, L.; Tang, Z.; Furniss, D.; Sakr, H.; Fang, Y.; Beres-Pawlik, E.; Benson, T.
20 M.; Seddon, A. B.; Sujecki, S., Mid-infrared emission in Tb³⁺-doped selenide glass fiber. *J.*
21 *Opt. Soc. Am. B* **2017**, *34*(3), A70-A79; (b) Starecki, F.; Braud, A.; Abdellaoui, N.; Doualan,
22 J.-L.; Boussard-Plédel, C.; Bureau, B.; Camy, P.; Nazabal, V., 7 to 8 μm emission from Sm³⁺
23 doped selenide fibers. *Opt. Express* **2018**, *26*(20), 26462-26469; (c) Starecki, F.; Abdellaoui,
24 N.; Braud, A.; Doualan, J.-L.; Boussard-Plédel, C.; Bureau, B.; Camy, P.; Nazabal, V., 8 μm
25 luminescence from a Tb³⁺ GaGeSbSe fiber. *Opt. Lett.* **2018**, *43*(6), 1211-1214.
- 26
27 14. (a) Starecki, F.; Braud, A.; Doualan, J.-L.; Ari, J.; Boussard-Plédel, C.; Michel, K.;
28 Nazabal, V.; Camy, P., All-optical carbon dioxide remote sensing using rare earth doped
29 chalcogenide fibers. *Optics and Lasers in Engineering* **2019**, *122*, 328-334; (b) Hafienne, I.;
30 Starecki, F.; Louvet, G.; Braud, A.; Doualan, J.-L.; Nazabal, V.; Camy, P. In *3.4 μm to 660 nm*
31 *wavelength conversion using Er³⁺ doped materials*, SPIE Photonics Europe, SPIE: 2018; p 8.
- 32
33 15. Nazabal, V.; Němec, P.; Jurdyc, A. M.; Zhang, S.; Charpentier, F.; Lhermite, H.;
34 Charrier, J.; Guin, J. P.; Moreac, A.; Frumar, M.; Adam, J. L., Optical waveguide based on
35 amorphous Er³⁺-doped Ga–Ge–Sb–S(Se) pulsed laser deposited thin films. *Thin Solid Films*
36 **2010**, *518*(17), 4941-4947.
- 37
38 16. Yan, K.; Vu, K.; Yang, Z.; Wang, R. P.; Debbarma, S.; Luther-Davies, B.; Madden, S.,
39 Emission properties of erbium-doped Ge-Ga-Se glasses, thin films and waveguides for laser
40 amplifiers. *Opt. Mater. Express* **2014**, *4*.
- 41
42 17. (a) Nazabal, V.; Starecki, F.; Doualan, J. L.; Němec, P.; Camy, P.; Lhermite, H.;
43 Bodiou, L.; Anne, M. L.; Charrier, J.; Adam, J. L., Luminescence at 2.8 μm: Er³⁺-doped
44 chalcogenide micro-waveguide. *Optical Materials* **2016**, *58*, 390-397; (b) Ramachandran, S.;
- 45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 Bishop, S. G., Excitation of Er³⁺ emission by host glass absorption in sputtered films of Er-
5 doped Ge₁₀As₄₀Se₂₅S₂₅ glass. *Applied Physics Letters* **1998**, *73* (22), 3196-3198.

6
7 18. (a) Frantz, J. A.; Shaw, L. B.; Myers, J. D.; Ewing, K. J.; Sanghera, J. S. In *Mid-IR*
8 *Emission in Erbium-Doped Gallium Lanthanum Sulfide Glass Integrated Optic Waveguides*,
9 2014 IEEE Photonics Society Summer Topical Meeting Series, 14-16 July 2014; 2014; pp 49-
10 50; (b) Bodiou, L.; Starecki, F.; Lemaitre, J.; Nazabal, V.; Doualan, J.-L.; Baudet, E.; Chahal,
11 R.; Gutierrez-Arroyo, A.; Dumeige, Y.; Hardy, I.; Braud, A.; Soulard, R.; Camy, P.; Němec,
12 P.; Palma, G.; Prudeniano, F.; Charrier, J., Mid-infrared guided photoluminescence from
13 integrated Pr³⁺-doped selenide ridge waveguides. *Optical Materials* **2018**, *75* (Supplement C),
14 109-115; (c) Louvet, G.; Normani, S.; Bodiou, L.; Gutwirth, J.; Lemaitre, J.; Pirasteh, P.;
15 Doualan, J.-L.; Benardais, A.; Ledemi, Y.; Messaddeq, Y.; Němec, P.; Charrier, J.; Nazabal,
16 V., Co-sputtered Pr³⁺-doped Ga-Ge-Sb-Se active waveguides for mid-infrared operation. *Opt.*
17 *Express* **2020**, *28* (15), 22511-22523; (d) Bodiou, L.; Baillieul, M.; Nazabal, V.; Lemaitre, J.;
18 Benardais, A.; Meziani, S.; Lorrain, N.; Dumeige, Y.; Nemeč, P.; Charrier, J., Carbon dioxide
19 mid-infrared sensing based on Dy³⁺ doped chalcogenide waveguide photoluminescence. *Opt.*
20 *Lett.* **2023**, *48* (5), 1128-1131.

21
22 19. Halenkovič, T.; Baillieul, M.; Gutwirth, J.; Němec, P.; Nazabal, V., Amorphous Ge-
23 Sb-Se-Te chalcogenide films fabrication for potential environmental sensing and nonlinear
24 photonics. *Journal of Materiomics* **2022**, *8* (5), 1009-1019.

25
26 20. Baudet, E.; Cardinaud, C.; Girard, A.; Rinnert, E.; Michel, K.; Bureau, B.; Nazabal, V.,
27 Structural analysis of RF sputtered Ge-Sb-Se thin films by Raman and X-ray photoelectron
28 spectroscopies. *Journal of Non-Crystalline Solids* **2016**, *444*, 64-72.

29
30 21. Weszka, J.; Daniel, P.; Burian, A. M.; Burian, A.; Elechower, M.; Nguyen, A. T., Raman
31 scattering in amorphous films of In_{1-x}Sex alloys. *Journal of Non-Crystalline Solids* **2003**, *315*
32 (3), 219-222.

33
34 22. Němec, P.; Olivier, M.; Baudet, E.; Kalendová, A.; Benda, P.; Nazabal, V., Optical
35 properties of (GeSe₂)_{100-x}(Sb₂Se₃)_x glasses in near- and middle-infrared spectral regions.
36 *Materials Research Bulletin* **2014**, *51*, 176-179.

37
38 23. Sójka, Ł.; Tang, Z.; Zhu, H.; Bereś-Pawlik, E.; Furniss, D.; Seddon, A. B.; Benson, T.
39 M.; Sujecki, S., Study of mid-infrared laser action in chalcogenide rare earth doped glass with
40 Dy³⁺, Pr³⁺ and Tb³⁺. *Opt. Mater. Express* **2012**, *2* (11), 1632-1640.

41
42 24. Sójka, L.; Tang, Z.; Furniss, D.; Sakr, H.; Oladeji, A.; Bereś-Pawlik, E.; Dantanarayana,
43 H.; Faber, E.; Seddon, A. B.; Benson, T. M.; Sujecki, S., Broadband, mid-infrared emission
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 from Pr³⁺ doped GeAsGaSe chalcogenide fiber, optically clad. *Optical Materials* **2014**, *36*(6),
5 1076-1082.

6
7 25. Sojka, L.; Tang, Z.; Jayasuriya, D.; Shen, M.; Nunes, J.; Furniss, D.; Farries, M.;
8 Benson, T. M.; Seddon, A. B.; Sujecki, S., Milliwatt-Level Spontaneous Emission Across the
9 3.5–8 μm Spectral Region from Pr³⁺ Doped Selenide Chalcogenide Fiber Pumped with a Laser
10 Diode. *Applied Sciences* **2020**, *10*(2), 539.

11
12 26. Sakr, H.; Furniss, D.; Tang, Z.; Sojka, L.; Moneim, N. A.; Barney, E.; Sujecki, S.;
13 Benson, T. M.; Seddon, A. B., Superior photoluminescence (PL) of Pr³⁺-In, compared to Pr³⁺-
14 Ga, selenide-chalcogenide bulk glasses and PL of optically-clad fiber. *Opt. Express* **2014**, *22*
15 (18), 21236-21252.

16
17 27. Sójka, L.; Tang, Z.; Furniss, D.; Sakr, H.; Bereś-Pawlik, E.; Seddon, A. B.; Benson, T.
18 M.; Sujecki, S., Numerical and experimental investigation of mid-infrared laser action in
19 resonantly pumped Pr³⁺ doped chalcogenide fibre. *Optical and Quantum Electronics* **2016**, *49*
20 (1), 21.
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
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