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# Dy<sup>3+</sup> doped GaGeSbSe fiber long-wave infrared emission

F. Starecki<sup>a\*</sup>, G. Louvet<sup>b,c</sup>, J. Ari<sup>b,c</sup>, A. Braud<sup>a</sup>, J-L. Doualan<sup>a</sup>, R. Chahal<sup>b</sup>, I. Hafienne<sup>a</sup>, C. Boussard-Plédel<sup>b</sup>, V. Nazabal<sup>b</sup> and P. Camy<sup>a</sup>

<sup>a</sup>Laboratoire CIMAP UMR 6252 CEA-CNRS-ENSICAen, Université de Caen, 14050 Caen, France

<sup>b</sup>Institut des Sciences Chimiques de Rennes, (ISCR), UMR-CNRS 6226, Université de Rennes 1, France.

<sup>c</sup>COPL, Université Laval, Québec, Canada

## ABSTRACT

We report on the mid-wave infrared (MWIR) and long-wave infrared (LWIR) emissions of a 1000 ppm Dy<sup>3+</sup> doped Ga<sub>5</sub>Ge<sub>20</sub>Sb<sub>10</sub>Se<sub>65</sub> chalcogenide fiber. Following a short-wave infrared (SWIR) optical pumping at 0.92, 1.12 and 1.32 μm using commercial laser diodes, LWIR luminescence around 7.3 μm (<sup>6</sup>H<sub>7/2</sub> → <sup>6</sup>H<sub>9/2</sub> transition) was recorded for the first time to the best of our knowledge along with MWIR emissions around 4.3 μm and 5.4 μm with a Dy<sup>3+</sup> doped Ga<sub>5</sub>Ge<sub>20</sub>Sb<sub>10</sub>Se<sub>65</sub> fiber. Frequency dependent spectroscopic investigation clearly shows that this LWIR luminescence originates from the <sup>6</sup>H<sub>7/2</sub> manifold. Spectroscopic properties of this Dy<sup>3+</sup> doped material and the comparison with its equivalent sulfide Dy<sup>3+</sup>:Ga<sub>5</sub>Ge<sub>20</sub>Sb<sub>10</sub>S<sub>65</sub> glass are presented.

**Keywords:** Chalcogenide glasses, rare earth, infrared, optical fiber

\*florent.starecki@ensicaen.fr; phone +33231452566

## 1. INTRODUCTION

For infrared (IR) photonic applications, chalcogenide glasses properties offer a wide range of possibilities thanks to the combination of a transparency window in the LWIR (8-12  $\mu\text{m}$ ) spectral domain, consequence of its typical low phonon energy, and thermomechanical properties still allowing a convenient use with standard preparation techniques, e.g. fiber drawing or polishing steps [1, 2]. These glasses proved efficient for sensing applications like molecule fingerprint detection using fiber evanescent wave spectroscopy for instance [3]. Taking advantage of the molding properties of these glasses, 3D chalcogenide glass printing was recently demonstrated [4], enabling the fabrication of complex optical components. Also, these materials are compatible with deposition techniques such as magnetron sputtering, permitting the realization of rare earth (RE) doped infrared optical waveguides with single-mode optical propagation at 4.7  $\mu\text{m}$  [5]. The strong non-linear refractive index of these chalcogenide glasses also permits the development of original mid-infrared supercontinuum source emitting up to 13  $\mu\text{m}$  [6].

Also, these glasses can be efficiently doped with trivalent rare earth ions [7] making possible the development of fibered infrared fluorescence sources [8, 9] while the development of RE-doped fibered laser sources in the MWIR is an ongoing attractive research field [10]. The  $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$  glass host has a low band-gap energy, and its transparency domain spans from 1 to 11  $\mu\text{m}$ . The average phonon energy is about  $250\text{ cm}^{-1}$  [11], indicating a potential embedded RE emission up to 8  $\mu\text{m}$ . This type of LWIR emissions was demonstrated for both  $\text{Tb}^{3+}$  [12] and  $\text{Sm}^{3+}$  doped  $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$  glasses [13], respectively emitting around 8.0  $\mu\text{m}$  and 7.3  $\mu\text{m}$ . Embedded in such a glass host,  $\text{Dy}^{3+}$  ions could also provide potentially a 7.3  $\mu\text{m}$  emission ( ${}^6\text{H}_{7/2} \rightarrow {}^6\text{H}_{9/2}$  transition).  $\text{Dy}^{3+}$  is also known for generating two MWIR (4.3 and 5.4  $\mu\text{m}$ ) emissions. As a matter of fact, a 4.3  $\mu\text{m}$  laser operation has already been obtained in a  $\text{Dy}^{3+}$  doped  $\text{PbGa}_2\text{S}_4$  crystal, using a powerful 1.7  $\mu\text{m}$  pump laser diodes [14] now available. In glass fibers, laser operation at 2.8  $\mu\text{m}$  was reported in  $\text{Dy}^{3+}$  doped  $\text{InF}_3$  fiber [15].

The 4.3  $\mu\text{m}$  fluorescence of a  $\text{Dy}^{3+}$  doped  $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{S}_{65}$  fiber was already used for the development of a mid-IR carbon dioxide sensor based on  $\text{CO}_2$  absorption measurement at 4.3  $\mu\text{m}$  [16]. A second type of  $\text{CO}_2$  sensor was recently developed using this 4.3  $\mu\text{m}$  source to probe the gas concentration variation, but additionally implementing a MWIR-NWIR wavelength converter to create an all-optical  $\text{CO}_2$  detection [17].

This sulfide glass was chosen for its ability to generate an efficient 4.3  $\mu\text{m}$  luminescence following a 920 nm pumping, thanks to its low phonon energy ( $350\text{ cm}^{-1}$ ) and large transparency window. But reducing the phonon energy can allow closely spaced upper manifolds to initiate radiative emissions, which can be the case in a selenide glass host. In this work, we present the MWIR and LWIR emissions from 1000 ppm  $\text{Dy}^{3+}$  doped  $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$  chalcogenide fibers under 1.3  $\mu\text{m}$  and 1.12  $\mu\text{m}$  optical pumping. In particular, we present, for the first time to our knowledge, emissions from the  ${}^6\text{H}_{7/2}$  level at 1.1  $\mu\text{m}$  and 7.3  $\mu\text{m}$  in  $\text{Dy}^{3+}$  doped selenide fibers. The spectroscopic characterization of the low-lying manifolds involved in these transitions is presented and compared to the  $\text{Dy}^{3+}$  properties in the sulfide  $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{S}_{65}$  glass.

## 2. MATERIAL AND METHODS

The glasses were elaborated from high purity raw materials, and melted in sealed ampoules in a rocking furnace. The melt was water-quenched and annealed below  $T_g$  for some hours to decrease the glass internal stress. A more extensive glass preparation is detailed in [18]. Following this process, 1000 ppm  $Dy^{3+}$  doped  $Ga_5Ge_{20}Sb_{10}Se_{65}$  and  $Dy^{3+}:Ga_5Ge_{20}Sb_{10}S_{65}$  glass rods were elaborated, from which 350  $\mu m$  diameter single core fibers were drawn. The selenide preform has been developed using  $TeCl_4$  and  $MgO$  to specifically limit the presence of Ge-O bonds because it plays a very important role in the efficiency of emissions in the LWIR spectral range.. Also, the  $Dy^{3+}:Ga_5Ge_{20}Sb_{10}S(Se)_{65}$  glass structure analysis was performed through K-edge of Ge, Ga, S and  $L_{III}$ -edge of Dy EXAFS for sulfide glasses and by Raman scattering spectroscopic for both composition [18]. Absorption spectra were recorded using a Perkin-Elmer Lambda 1050 spectrophotometer. The emission experiments were carried out using three different laser diodes with optical power of few watts at the wavelengths of 0.92, 1.12 and 1.32  $\mu m$ , coupled to standard 105/125  $\mu m$  silica fibers. The chalcogenide fibers were mounted in FC/PC connectors and their end faces were polished. The IR signal at the fiber output was collimated using a C037TME-F lens (Thorlabs), and appropriate long-pass filters (Spectrogon) were used to remove any parasitic higher order contribution from the transmitted pump or SWIR  $Dy^{3+}$  luminescence. Adapted diffraction gratings were also used for each wavelength domain. For the fiber experiments, an incident power of 700 mW from the 1.3  $\mu m$  laser diode (Q-Photonics QSM-1320-4.5) was used, while for LWIR fluorescence experiments a 1.12  $\mu m$  laser diode (Innolume LD-1120-BA-6W) was used as pumping source (incident power of 1.6 W). Fluorescence spectra were corrected from the setup spectral response using a black-body-like source (Arcoptix MIR-2000-9000). Lifetimes experiments were performed on bulk samples using a Continuum Horizon OPO as pulsed laser source. SWIR luminescence was recorded using a thermoelectrically cooled InGaAs detector, while MWIR and LWIR spectra were recorded using a liquid-nitrogen cooled HgCdTe detector.

### 3. RESULTS AND DISCUSSION

#### 3.1 Fiber attenuation

In Figure 1 is reported the fiber attenuation comparison between the  $Dy^{3+}$ -doped  $Ga_5Ge_{20}Sb_{10}Se_{65}$  and its counterpart sulfide glass. Figure 1 also features the main impurities absorption bands, like S-H (4.0  $\mu m$ ) or Se-H (4.5  $\mu m$ ).

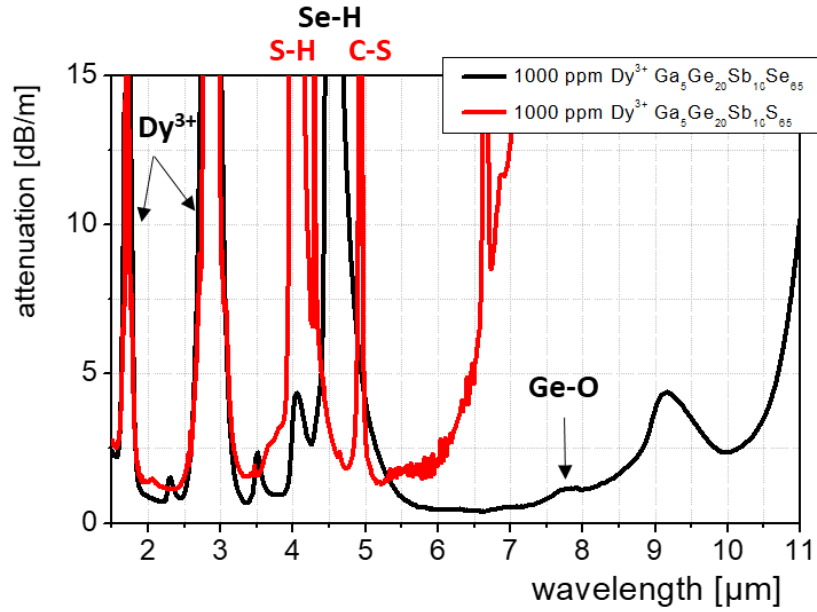


Figure 1: comparison of sulfide and selenide  $\text{Dy}^{3+}$  doped  $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}(\text{S or Se})_{65}$  fiber attenuation spectra.

The purification process using  $\text{TeCl}_4$  and  $\text{MgO}$  is assumed to lead to a significant reduction in the amount of  $\text{Ge-O}$  bonds within the selenide glass [Figure 1], which absorption peak is at  $7.7 \mu\text{m}$ . The background losses at this wavelength is  $1.2 \text{ dB/m}$ , which is a key issue for efficient LWIR luminescence generation and propagation since it is resonant with the  $\text{Dy}^{3+} {}^6\text{H}_{7/2} \rightarrow {}^6\text{H}_{9/2}$  emission. Figure 1 shows that the sulfide fiber multiphonon edge lies at  $7 \mu\text{m}$ , restricting the use of this material to MWIR applications.

### 3.2 Absorption properties and Judd-Ofelt analysis

The spectroscopic study of  $\text{Dy}^{3+}:\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$  is presented here and compared to the  $\text{Dy}^{3+}:\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{S}_{65}$  sulfide glass properties. The spectroscopic study for this  $\text{Dy}^{3+}$  doped sulfide glass was already reported [19]. For the  $\text{Dy}^{3+}:\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$  material, only a brief description of the emission properties could be found in [18], and thus we present here a comprehensive study of  $\text{Dy}^{3+}:\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$  including Judd-Ofelt calculations and fluorescence lifetimes measurements. In Figure 2(a) is reported the absorption cross-sections of the  $\text{Dy}^{3+}$  ion embedded in  $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{S}_{65}$  and  $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$  glass hosts, while Figure 2(b) shows the expected  $\text{Dy}^{3+}$  emissions in the sulfide and selenide matrices.

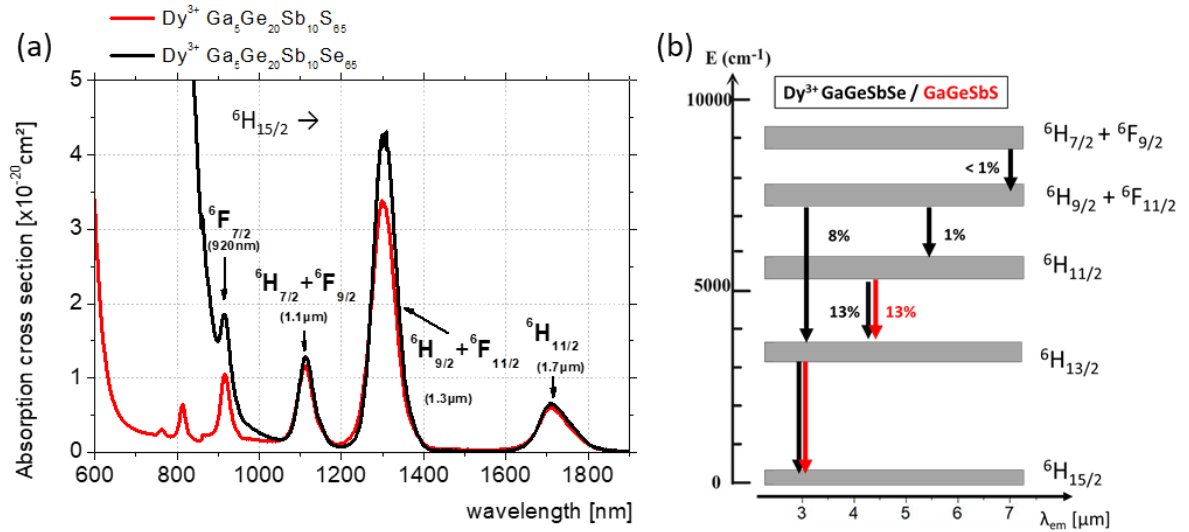


Figure 2: comparison of: (a) absorption cross-sections and (b) MWIR and LWIR expected emissions for the  $\text{Dy}^{3+}$ :  $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{S}_{95}$  and  $\text{Dy}^{3+}$ :  $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$  glasses.

Figure 2(a) indicates that  $\text{Dy}^{3+}$  absorption cross-sections are comparable from a sulfide to a selenide matrix. One can notice on one hand a difference for the  ${}^6\text{H}_{9/2} + {}^6\text{F}_{11/2}$  absorption band, with a peak value of  $4.2 \times 10^{-20} \text{ cm}^2$  in the selenide material. On the other hand,  $1.1 \mu\text{m}$  ( ${}^6\text{H}_{7/2} + {}^6\text{F}_{9/2}$ ) and  $1.3 \mu\text{m}$  ( ${}^6\text{H}_{11/2}$ ) absorption cross-sections are similar between the sulfide and selenide material. The  ${}^6\text{F}_{7/2}$  absorption band is at the edge of the selenide material transparency window, so that a significant power fraction will be directly converted into heat when pumping  $\text{Dy}^{3+}$  ions at 920 nm. Therefore, a special care must be taken when pumping at this wavelength so as to avoid optical damage on the fiber. Another possibility is to excite the  $\text{Dy}^{3+}$ : $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$  glass at longer wavelength than 920 nm to generate MWIR or LWIR emissions. The only available pumping band for LWIR luminescence generation from the  ${}^6\text{H}_{7/2}$  level is a direct excitation of this very same level at  $1.1 \mu\text{m}$ . For the MWIR luminescence at  $5.4 \mu\text{m}$  ( ${}^6\text{H}_{9/2} + {}^6\text{F}_{11/2} \rightarrow {}^6\text{H}_{11/2}$  transition) and at  $4.3 \mu\text{m}$  ( ${}^6\text{H}_{11/2} \rightarrow {}^6\text{H}_{13/2}$  transition) the direct pumping of the  ${}^6\text{H}_{9/2}$  level at  $1.3 \mu\text{m}$  is more efficient since the absorption cross-section is larger at  $1.3 \mu\text{m}$  than at  $1.1 \mu\text{m}$ .

Some MWIR and all LWIR transitions are dominated by non-radiative relaxations within a sulfide glass host because of its larger phonon energy than in a selenide material [18]. The multiphonon relaxation rates for sulfide glasses, given in [20], indicates that the  ${}^6\text{H}_{7/2}$  and  ${}^6\text{H}_{9/2}$  manifolds luminescence is quenched so that the MWIR emissions are limited to the  ${}^6\text{H}_{11/2} \rightarrow {}^6\text{H}_{13/2}$  transition at  $4.3 \mu\text{m}$  and  ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$  transition at  $2.8 \mu\text{m}$ . For the  $\text{Dy}^{3+}$ -doped selenide material, the lower phonon energy reduces the multiphonon relaxation rates for both  ${}^6\text{H}_{7/2}$  and  ${}^6\text{H}_{9/2}$  manifolds (for the sake of clarity the mention of the combined  ${}^6\text{F}_{9/2}$  and  ${}^6\text{F}_{11/2}$  levels will be implicit in the rest of the text). These two latter manifolds can thus potentially give rise to MWIR to LWIR emissions when considering the  ${}^6\text{H}_{7/2} - {}^6\text{H}_{9/2}$  and  ${}^6\text{H}_{9/2} - {}^6\text{H}_{11/2}$  energy gaps [Figure 2(b)].

From the  $\text{Dy}^{3+}$ : $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$  cross-section calibrated absorption spectrum, the Judd-Ofelt (JO) parameters were calculated to have an assessment of the radiative lifetimes and branching ratios. A standard fitting procedure was used to derive the  $\Omega_{2,4,6}$  parameters which reproduce the integrated absorption band values while taking into account magnetic dipole contributions [21]. The four  ${}^6\text{H}_{7/2; 9/2}$ :

${}_{11/2; 13/2}$  integrated absorption bands were considered as input data for this JO analysis. The  ${}^6F_{7/2}$  absorption band was not considered since it lies at the edge of the bandgap [Figure 2(a)]. The corresponding Judd-Ofelt  $\Omega_{2,4,6}$  parameters are (9.6; 2.9; 2.4) ( $\times 10^{-20}$  cm<sup>2</sup>). The radiative lifetimes and branching ratios were then calculated with this set of  $\Omega_{2,4,6}$  parameters and are reported in Table 1.

**Table 1. Dy<sup>3+</sup> Ga<sub>5</sub>Ge<sub>20</sub>Sb<sub>10</sub>Se<sub>65</sub> transition average wavelength, radiative lifetimes and branching ratios ( $\beta$ ) derived from the Judd-Ofelt analysis.**

Manifolds		$\lambda_{av}$ [ $\mu$ m]	$\tau_{rad}(JO)$ [ms]	$\beta$
From	To			
${}^6H_{7/2} + {}^6F_{9/2}$	${}^6H_{9/2} + {}^6F_{11/2}$	7.52	0.13	0.004
	${}^6H_{11/2}$	3.18		0.03
	${}^6H_{13/2}$	1.81		0.31
	${}^6H_{15/2}$	1.11		0.65
${}^6H_{9/2} + {}^6F_{11/2}$	${}^6H_{11/2}$	5.51	0.11	0.01
	${}^6H_{13/2}$	2.38		0.08
	${}^6H_{15/2}$	1.30		0.91
${}^6H_{11/2}$	${}^6H_{13/2}$	4.21	1.63	0.13
	${}^6H_{15/2}$	1.71		0.87
${}^6H_{13/2}$	${}^6H_{15/2}$	2.88	4.17	1.00

The radiative lifetimes and branching ratios presented in Table 1 should be compared to the same parameters derived for its sulfide counterpart Dy<sup>3+</sup>:Ga<sub>5</sub>Ge<sub>20</sub>Sb<sub>10</sub>S<sub>65</sub> [19]. The Dy<sup>3+</sup> radiative lifetimes are found to be longer in the selenide matrix, except for the  ${}^6H_{13/2}$  manifold, while branching ratios are quite comparable in the sulfide and selenide hosts. Considering now the MWIR and LWIR emission potentialities of the Dy<sup>3+</sup>:Ga<sub>5</sub>Ge<sub>20</sub>Sb<sub>10</sub>Se<sub>65</sub> fibers, it is worth noticing that the  ${}^6H_{7/2} \rightarrow {}^6H_{9/2}$  (7.3  $\mu$ m) has a poor branching ratio of 0.4%. However, Sm<sup>3+</sup> doped Ga<sub>5</sub>Ge<sub>20</sub>Sb<sub>10</sub>Se<sub>65</sub> glasses exhibit a clear LWIR emission around 7.4  $\mu$ m with a similar branching ratio [13], so that one could expect to observe the Dy<sup>3+</sup> emission at 7.3  $\mu$ m.

The MWIR  ${}^6H_{9/2} \rightarrow {}^6H_{11/2}$  transition around 5.4  $\mu$ m has also a weak branching ratio of 1%, but this emitting level can be efficiently pumped directly owing to the strong  ${}^6H_{15/2} \rightarrow {}^6H_{9/2}$  absorption (1.3  $\mu$ m). The other Dy<sup>3+</sup> MWIR emission is the 4.3  $\mu$ m emission ( ${}^6H_{11/2} \rightarrow {}^6H_{13/2}$ ), which is commonly observed in sulfide doped fiber and can be advantageously used for CO<sub>2</sub> detection for instance [19].

### 3.3 Lifetime measurements

Table 2 shows the fluorescence Dy<sup>3+</sup> lifetimes measured in a 1000 ppm doped Dy<sup>3+</sup>:Ga<sub>5</sub>Ge<sub>20</sub>Sb<sub>10</sub>Se<sub>65</sub> glass, compared to the equivalent sulfide glass.

**Table 2. 1000 ppm doped Dy<sup>3+</sup> Ga<sub>5</sub>Ge<sub>20</sub>Sb<sub>10</sub>(Se<sub>65</sub> or S<sub>65</sub>) experimental fluorescence lifetimes.**

manifold	Sulfide [18]	selenide
${}^6H_{7/2}$	3 $\mu$ s	42 $\mu$ s
${}^6H_{9/2}$	34 $\mu$ s	230 $\mu$ s
${}^6H_{11/2}$	1.3 ms	1.46 ms
${}^6H_{13/2}$	5.6 ms	3.3 ms

The fluorescence lifetimes of the Dy<sup>3+</sup>  ${}^6H_{7/2}$  and  ${}^6H_{9/2}$  manifolds in the selenide glass are one order of magnitude longer than the ones in its sulfide glass counterpart. The  ${}^6H_{7/2}$  and  ${}^6H_{9/2}$  manifolds

fluorescence lifetimes goes from 3 to 42  $\mu\text{s}$  and from 34 to 230  $\mu\text{s}$  respectively. This lengthening of the lifetimes clearly illustrates the reduction of the phonon energy when going from a sulfur to a selenium based compound.

For the  ${}^6\text{H}_{11/2}$  and  ${}^6\text{H}_{13/2}$  manifolds, the measured fluorescence lifetimes are comparable in both hosts which can be expected since the  ${}^6\text{H}_{11/2}$  to  ${}^6\text{H}_{13/2}$  and  ${}^6\text{H}_{13/2}$  to  ${}^6\text{H}_{15/2}$  energy gaps are about 2350 and 3450  $\text{cm}^{-1}$  respectively. These energy gaps are quite large compared to the 350  $\text{cm}^{-1}$  and 250  $\text{cm}^{-1}$  of the sulfide and selenide host respectively meaning that the  ${}^6\text{H}_{11/2}$  and  ${}^6\text{H}_{13/2}$  are weakly affected by multiphonon relaxation processes.

### 3.4 MWIR luminescence

In this section, we will describe the luminescence properties of  $\text{Dy}^{3+}:\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$  fibers in the MWIR spectral domain. Figure 3(a) presents a comparison between a sulfide and selenide fiber with the same 120 mm length and the same 1000 ppm  $\text{Dy}^{3+}$  doping level. Following a 1.3  $\mu\text{m}$  optical pumping with the same incident power of 700 mW. Figure 3(b) shows the 1.3  $\mu\text{m}$  pumping and energy levels involved in this cascade luminescence process.

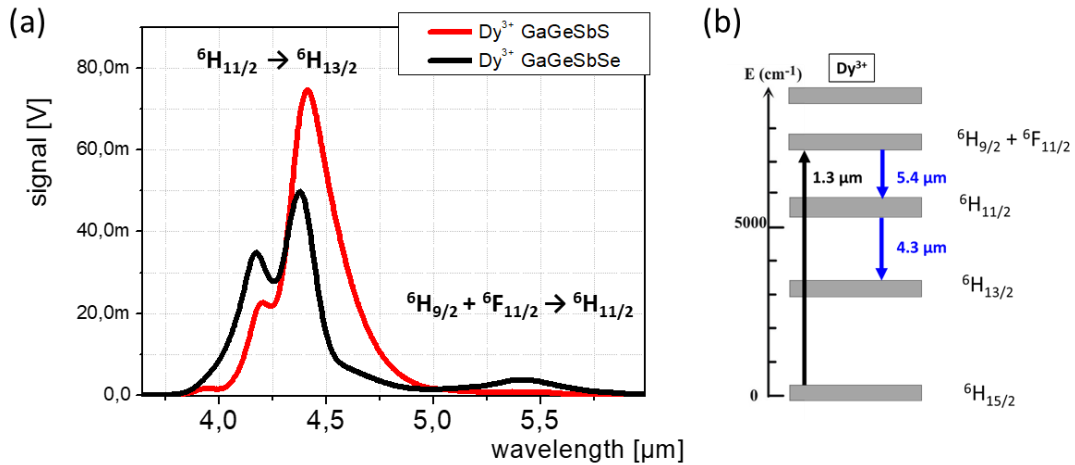


Figure 3: (a) 1000 ppm  $\text{Dy}^{3+}:\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$  and 1000 ppm  $\text{Dy}^{3+}:\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{S}_{65}$  luminescence measurements for a 1320 nm pumping; (b) energy diagram and pumping scheme for the  $\text{Dy}^{3+}$  MWIR transitions.

The first noticeable MWIR emission band is the  ${}^6\text{H}_{11/2} \rightarrow {}^6\text{H}_{13/2}$  transition around 4.3  $\mu\text{m}$ ). One can notice that the sulfide and selenide glass host do not exhibit the same emission line shape and this is most likely due to Se-H and S-H bonds absorption. As indicated in the fiber attenuation spectra [Figure 1], S-H and Se-H bonds absorption peaks are located at 4.0 and 4.5  $\mu\text{m}$ , respectively. Therefore, the shorter wavelength part of the emission spectrum around 4  $\mu\text{m}$  in the sulfide glass is truncated by the S-H absorption while it is the longer wavelength part in the selenide host which is affected by the Se-H absorption. As a result, the  $\text{Dy}^{3+}$ -doped fiber luminescence central emission wavelength is shifted from 4.34  $\mu\text{m}$  to 4.43  $\mu\text{m}$  from the selenide to the sulfide glass host. Figure 3(a) features the  ${}^6\text{H}_{9/2} \rightarrow {}^6\text{H}_{11/2}$  MWIR emission around 5.4  $\mu\text{m}$  following the 1.3  $\mu\text{m}$  pumping. This emission is recorded with a clear satisfactory signal to noise ratio in the selenide glass, whereas for the sulfide glass the emission intensity is one order of magnitude lower. Considering the shorter  ${}^6\text{H}_{9/2}$



fluorescence lifetime of 34  $\mu\text{s}$  in the sulfide host compared to the 230  $\mu\text{s}$  recorded in the selenide glass, this low fluorescence intensity is to be expected.

Emission spectra are corrected from the setup spectral response, so that the 4.3 and 5.4  $\mu\text{m}$  emission intensities can be compared in each glass. Because of its poor branching ratio ( $\beta=1\%$ ), the 5.4  $\mu\text{m}$  ( ${}^6\text{H}_{9/2} \rightarrow {}^6\text{H}_{11/2}$  transition) intensity is lower than the 4.3  $\mu\text{m}$  ( ${}^6\text{H}_{11/2} \rightarrow {}^6\text{H}_{13/2}$ ) ( $\beta = 13\%$ ). Additionally, as discussed earlier, the  ${}^6\text{H}_{9/2}$  is more quenched by multiphonon relaxation than the  ${}^6\text{H}_{11/2}$  level further reducing the intensity at 5.4  $\mu\text{m}$  compared to 4.3  $\mu\text{m}$ . Following the 1.3 $\mu\text{m}$  pumping, the  $\text{Dy}^{3+}$  excitation into the  ${}^6\text{H}_{11/2}$  manifold is thus mostly due to this multiphonon relaxation from the  ${}^6\text{H}_{9/2}$  level explaining why the 4.3  $\mu\text{m}$  emission intensities are comparable in both glasses. Moreover, since the  $\text{Dy}^{3+}$  doping level and fiber lengths are identical in Figure 3, one can compare the 4.3  $\mu\text{m}$  intensities from the two fibers. The sulfide fiber exhibits a higher intensity despite a slightly lower 1.3  $\mu\text{m}$  absorption cross-section (Figure 2(a)). This illustrates the consequence of the 100  $\text{cm}^{-1}$  shift of the glass host phonon energy from the selenide to the sulfide based chalcogenide glass leading to a higher multiphonon relaxation rate in the sulfide glass from the  ${}^6\text{H}_{9/2}$  to the  ${}^6\text{H}_{11/2}$  and thus to a larger  ${}^6\text{H}_{11/2}$  population and subsequent 4.3  $\mu\text{m}$  intensity. Under the same pumping conditions, a sulfide fiber is thus preferable to generate luminescence at 4.3  $\mu\text{m}$ , while for an emission at 5.4  $\mu\text{m}$  the  $\text{Dy}^{3+}$ -doped selenide material is more suitable.

### 3.5 LWIR luminescence

A practical way to assess the possibility to observe a LWIR luminescence is to record first the SWIR emission from the same emitting level, as illustrated in a previous LWIR study of  $\text{Sm}^{3+}$  doped selenide fibers [13]. In  $\text{Dy}^{3+}$  doped materials, the LWIR emission is expected to arise from the  ${}^6\text{H}_{7/2}$  manifold. Consequently, the first step is to record the SWIR emission from this manifold around 1.15  $\mu\text{m}$  ( ${}^6\text{H}_{7/2} \rightarrow {}^6\text{H}_{15/2}$  transition). Figure 4 shows the  ${}^6\text{H}_{7/2}$  and  ${}^6\text{H}_{9/2}$  emissions recorded in the SWIR domain under optical pumping at 920 nm. A low pumping power (80 mW at 920 nm) was used to avoid optical damage on the fiber by the pump beam since the  ${}^6\text{H}_{15/2} \rightarrow {}^6\text{F}_{7/2}$  absorption band lies on the edge of the band-gap (Figure 2(a)). The  ${}^6\text{H}_{7/2} \rightarrow {}^6\text{H}_{15/2}$  transition has the highest branching ratio of the  ${}^6\text{H}_{7/2}$  transitions ( $\beta=65\%$ ), creating favorable conditions to record this emission.

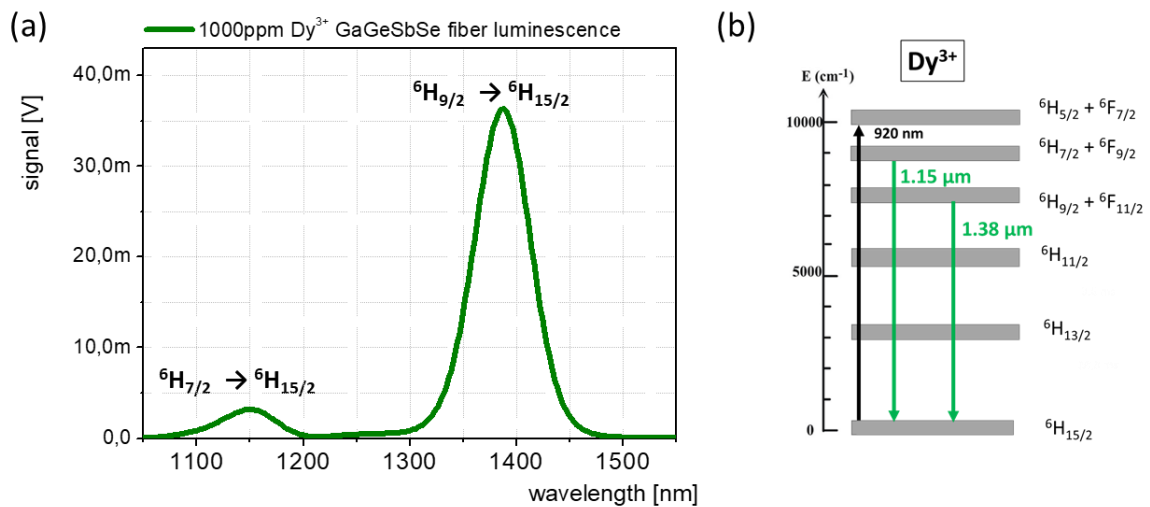


Figure 4: (a) SWIR luminescence of the 1000 ppm  $\text{Dy}^{3+}$  doped  $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$  fiber following a 920 nm optical pumping; (b) pumping scheme and SWIR emission line of the  $\text{Dy}^{3+}$  ion.

Thus, despite a low pumping power, the 1.15  $\mu\text{m}$  emission from the  ${}^6\text{H}_{7/2}$  level is clearly observed in Figure 4(a). This emission shows that the  ${}^6\text{H}_{7/2}$  level is not quenched [Figure 4(b)] and represents promising evidence that the 7.3  $\mu\text{m}$  emission ( ${}^6\text{H}_{7/2} \rightarrow {}^6\text{H}_{9/2}$  transition) can be recorded. However, the small energy gap between the  ${}^6\text{H}_{7/2}$  and  ${}^6\text{H}_{9/2}$  manifolds clearly indicates that the  ${}^6\text{H}_{7/2}$  decay is dominated by multiphonon relaxation processes. A clear evidence of this non-radiative process dominance is the strong 1.4  $\mu\text{m}$  emission from the  ${}^6\text{H}_{9/2}$  manifold depicted in Figure 4(a). Under this 920 nm pumping, the  ${}^6\text{H}_{9/2}$  level is indeed only populated through non-radiative decay from the  ${}^6\text{H}_{7/2}$  excited state. Following this motivating result obtained in the SWIR spectral region, the LWIR luminescence properties of the 1000 ppm  $\text{Dy}^{3+}$  doped  $\text{Ga}_5\text{Ge}_{20}\text{Sb}_{10}\text{Se}_{65}$  fiber were investigated and are reported in Figure 5.

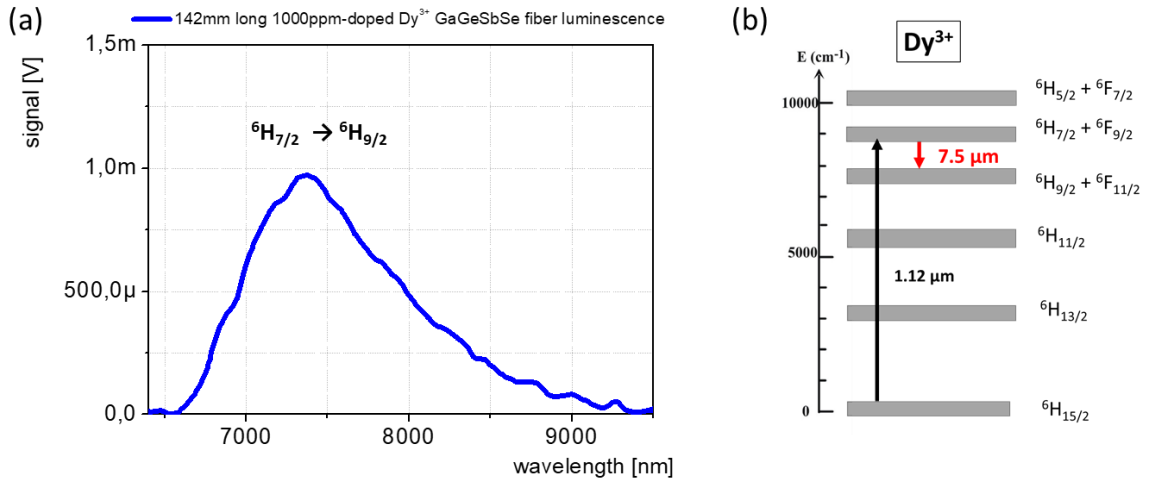


Figure 5: (a) LWIR luminescence of the  $\text{Dy}^{3+}$  ( ${}^6\text{H}_{7/2} \rightarrow {}^6\text{H}_{9/2}$ ) ion in the  $\text{GaGeSbSe}$  system; (b) pumping scheme and LWIR emission line of the  $\text{Dy}^{3+}$  ion.

Figure 5(a) shows the LWIR luminescence of the  $\text{Dy}^{3+}$  doped selenide fiber spanning from 6.7 to 9  $\mu\text{m}$ . The optimal fiber length for this LWIR emission depends on the propagation losses at the pump and LWIR wavelengths. Thus, after optimization of the fiber lengths, we obtained the highest LWIR emission intensity for a 142 mm long fiber, which corresponds to 93% absorption of the pump signal. The purification of this selenide fiber is assumed to limit background losses in the LWIR domain caused by the absorption from stretching vibrational modes of the Ge-O bonds. This absorption band around 7.8  $\mu\text{m}$  is critical regarding the LWIR  $\text{Dy}^{3+}$  luminescence as it precisely re-absorbs the generated fluorescence [Figure 2(b)]. Therefore, the removal of Ge-O bonds from the glass structure network is strongly required to achieve a  $\text{Dy}^{3+}$  LWIR luminescence.

To further evidence the fact that this LWIR luminescence truly originates from the  ${}^6\text{H}_{7/2}$ , we recorded the intensity drop of the 1.15 ( ${}^6\text{H}_{7/2}$ ), 1.4 ( ${}^6\text{H}_{9/2}$ ) and 7.3  $\mu\text{m}$  emission lines as a function of the pump modulation frequency. The  ${}^6\text{H}_{7/2}$  and  ${}^6\text{H}_{9/2}$  levels exhibit different fluorescence lifetimes (42 and 230  $\mu\text{s}$  respectively in Table 2). Thus, the  ${}^6\text{H}_{9/2} \rightarrow {}^6\text{H}_{15/2}$  emission intensity is expected to decrease faster than the  ${}^6\text{H}_{7/2} \rightarrow {}^6\text{H}_{15/2}$  emission intensity when increasing the pump modulation frequency [Figure 6].

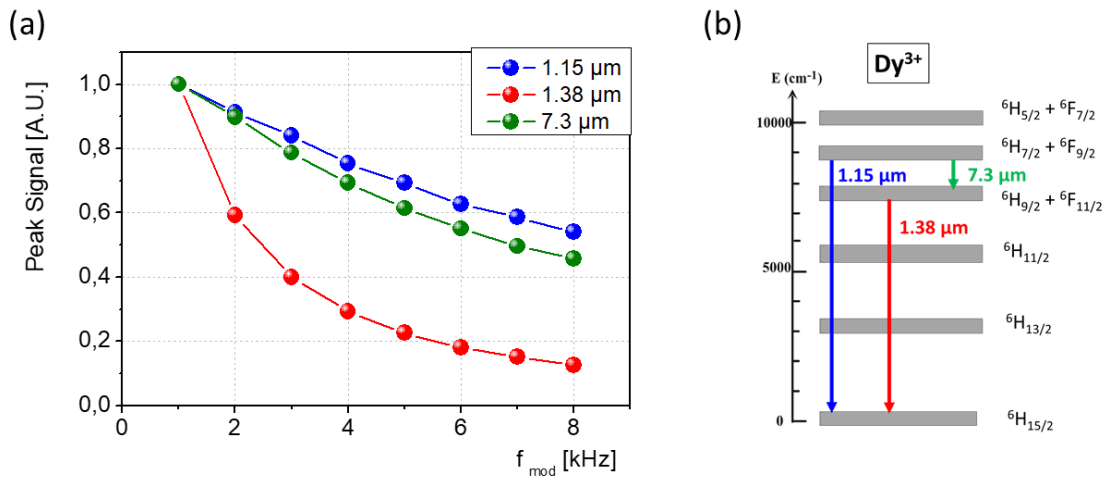


Figure 6: (a) normalized luminescence intensities of the 1.15, 1.4 and 7.3 μm emissions as a function of the pump modulation frequency; (b) Dy<sup>3+</sup> level scheme showing the investigated transitions.

The 1/e fluorescence intensity drop is expected to be at 24 kHz ( $\tau_{\text{fluo}} = 42 \mu\text{s}$ ,  $\tau_{\text{fluo}}^{-1} = 24 \text{ kHz}$ ) and 4.3 kHz ( $\tau_{\text{fluo}} = 230 \mu\text{s}$ ,  $\tau_{\text{fluo}}^{-1} = 4.3 \text{ kHz}$ ) for the  ${}^6\text{H}_{7/2}$  and  ${}^6\text{H}_{9/2}$  levels respectively. For the  ${}^6\text{H}_{9/2}$  manifold emission recorded at 1.4 μm ( ${}^6\text{H}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ ), the intensity drop in Figure 6(a) is likely faster than at 1.15 μm ( ${}^6\text{H}_{7/2}$  emission). The 1/e intensity decrease for the  ${}^6\text{H}_{9/2}$  level expected at 4.3 kHz is in a fairly good agreement [Figure 6]. More importantly, Figure 6(a) clearly shows that the 1.15 μm ( ${}^6\text{H}_{7/2} \rightarrow {}^6\text{H}_{15/2}$ ) and 7.3 μm ( ${}^6\text{H}_{7/2} \rightarrow {}^6\text{H}_{9/2}$ ) normalized intensities present the same relative decrease, showing that these two emissions originate from the same  ${}^6\text{H}_{7/2}$  manifold.

Finally, a raw luminescence intensity comparison of the LWIR emissions of Tb<sup>3+</sup>, Sm<sup>3+</sup> and Dy<sup>3+</sup> embedded in the Ga<sub>5</sub>Ge<sub>20</sub>Sb<sub>10</sub>Se<sub>65</sub> glass host was investigated and presented in Figure 7. Sm<sup>3+</sup> and Tb<sup>3+</sup> spectra are taken from [13], and were recorded in the same conditions with the same setup as detailed in [13].

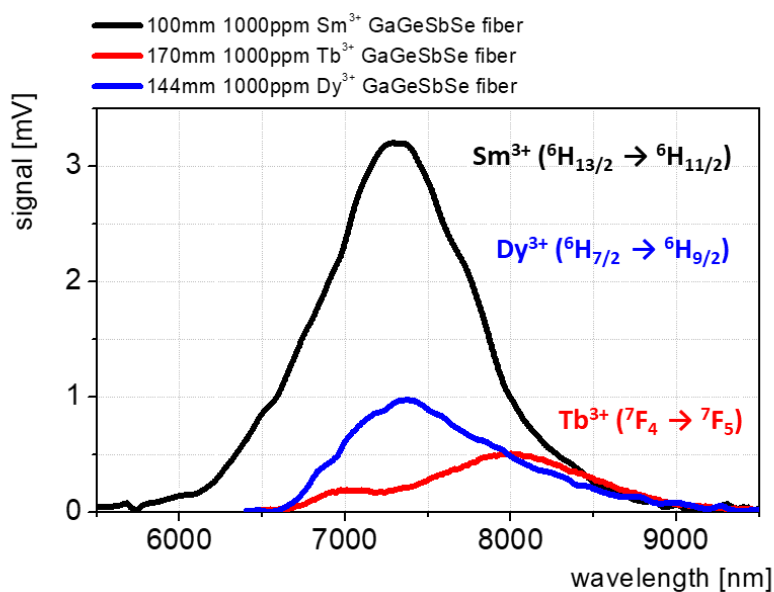


Figure 7: LWIR luminescence spectra for the Tb<sup>3+</sup>, Sm<sup>3+</sup> and Dy<sup>3+</sup> ions in the Ga<sub>5</sub>Ge<sub>20</sub>Sb<sub>10</sub>Se<sub>65</sub> glass host, intensities are corrected from the absorbed pump power

The Sm<sup>3+</sup> and Dy<sup>3+</sup> spectra emission spectra presented in Figure 7 were obtained with the same setup. The absorbed power was about 93% for the 144 mm long Dy<sup>3+</sup> doped fiber and of 90% for the Sm<sup>3+</sup> doped fiber. Figure 7 clearly shows that the Sm<sup>3+</sup> emission is more than three times higher than the Dy<sup>3+</sup> one. This is mainly due to the branching ratio difference, with a  $\beta$  value of 8% for the Sm<sup>3+</sup> <sup>6</sup>H<sub>13/2</sub> → <sup>6</sup>H<sub>11/2</sub> transition and less than the percent for the Dy<sup>3+</sup> <sup>6</sup>H<sub>7/2</sub> → <sup>6</sup>H<sub>9/2</sub> transition. Tb<sup>3+</sup> and Dy<sup>3+</sup> ions show comparable intensities for a similar absorbed pump power, with maximum emission wavelengths of 8.0 and 7.3  $\mu$ m respectively.

#### 4. CONCLUSION

1000 ppm Dy<sup>3+</sup> doped Ga<sub>5</sub>Ge<sub>20</sub>Sb<sub>10</sub>Se<sub>65</sub> glass preform and fibers were elaborated from conventional methods, with enhanced purification techniques. The 7.3  $\mu$ m centered LWIR luminescence (<sup>6</sup>H<sub>7/2</sub> → <sup>6</sup>H<sub>9/2</sub> transition) from these fibers is demonstrated here for the first time to our knowledge. Alongside, a comprehensive spectroscopic study of this Dy<sup>3+</sup> doped selenium based glass is presented. Absorption cross-sections and Judd-Ofelt analysis were investigated and the fluorescence lifetimes of the different emitting levels, in particular the <sup>6</sup>H<sub>7/2</sub> level, were measured. Emission spectra were compared with the Dy<sup>3+</sup> doped equivalent sulfide glass, illustrating the Dy<sup>3+</sup> emissions phonon energy dependency in the MWIR spectral domain. The highest LWIR luminescence intensity was achieved using a 142 mm long 1000 ppm Dy<sup>3+</sup> doped Ga<sub>5</sub>Ge<sub>20</sub>Sb<sub>10</sub>Se<sub>65</sub> fiber under 1.12  $\mu$ m pumping.

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