

# LOW PHONON CONCENTRATION LASING GLASSES FOR 1.3 $\mu\text{m}$ AMPLIFICATION

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## 1 ABSTRACT

Ge-Ga-S-glasses doped with 15000 mole-ppm  $\text{Pr}^{3+}$  have been developed for applications in optical amplifiers for 1.3  $\mu\text{m}$ . The formation of crystalline phase separations in  $\text{Ge}_{25}\text{Ga}_{10}\text{S}_{65}$  could be suppressed by modification of the glass composition with Sb. Samples have been prepared by melting in sealed silica ampoules at 950 °C. Ge-Ga-Sb-S-glasses, doped with 15000 mole ppm  $\text{Pr}^{3+}$ , were synthesized by addition of  $\text{Sb}_2\text{S}_3$  up to contents of 14.3 mole% to the composition  $\text{Ge}_{25}\text{Ga}_{10}\text{S}_{65}$  (corresponding to  $83,3\text{GeS}_2\text{-}16,7\text{Ga}_2\text{S}_3$ ) or by replacing up to 50 mole% of Ga by Sb. Transparent to opaque glasses were obtained which were free from crystalline phase separations. The modification of the glasses with Sb leads to a remarkable decrease of the transformation temperature of the glasses. However, the temperature working range remains almost unaffected. The transparent glasses exhibit with 15 - 18  $\mu\text{s}$  the same fluorescence lifetimes and the same fluorescence maximum position (1340 - 1341 nm) and FWHM (63 nm) as the unmodified Ge-Ga-S-glass. The preparation process for both glass systems could be optimized to obtain monoliths with lengths of several centimeters and intrinsic optical losses of only 0.05 dB/cm at 1.3  $\mu\text{m}$  (after correction of reflection), which is of very high importance for the future development of planar amplifiers with remarkable net gain.

## 2 INTRODUCTION

The  ${}^1\text{G}_4\text{-}{}^3\text{H}_5$ -transition of  $\text{Pr}^{3+}$  in appropriate host glasses is used in optical amplifiers for the 1.3  $\mu\text{m}$  wavelength range. Up to now, only expensive fiber amplifiers with lengths of more than 10 meters and  $\text{Pr}^{3+}$  concentrations between 500 and 1,000 ppm  $\text{Pr}^{3+}$  are available [1,2]. Planar waveguide amplifiers are required for optical networks and could be integrated in optical switching units for the compensation of internal losses. Simulations for a waveguide amplifier of a length of 5 cm and a cross section of  $3\mu\text{m} \times 3\mu\text{m}$  showed that the maximum amplification is expected at a  $\text{Pr}^{3+}$ -dopant concentration of 15,000 ppm [3].

Therefore, glasses with a high  $\text{Pr}^{3+}$ -solubility have to be developed, exhibiting a long  ${}^1\text{G}_4$  fluorescence lifetime [3,4] and low optical losses between 1  $\mu\text{m}$  and 1.4  $\mu\text{m}$ . Long fluorescence lifetimes can be obtained by minimizing the multiphonon relaxation due to the incorporation of the  $\text{Pr}^{3+}$  into a host with low phonon energy [5]. Therefore,  $\text{Pr}^{3+}$  doped sulfide glasses have been investigated intensively in the last few years with respect to a fabrication of optical amplifiers [4,6-12]. Their advantages compared with fluoride glasses are a better chemical durability and longer fluorescence lifetimes because of their lower phonon energy [4]. The published data about fluorescence lifetimes of  $\text{Pr}^{3+}$ -doped sulfide glasses refer mostly to low dopant concentrations ( $\leq 1000$  ppm) [4,6-9]. This also concerns patents about rare earth doped sulfide glasses, in which glass compositions with contents up to 6 mole% rare earth sulfide are claimed, fluorescence data however are only given for example compositions containing  $\text{Pr}^{3+}$  in low dopant concentrations [10-12]. Only a few glass systems with  $\text{Pr}^{3+}$ -concentrations of 10,000 ppm and more have been reported in the literature. These are  $\text{Pr}^{3+}$ -doped La-Ga-S-glasses [6],  $\text{Ge}_{25}\text{Ga}_5\text{S}_{70}$ -glasses [4] and Ge-Ga-Ba-S glasses [9]. Data about optical attenuation or microstructural characterization with respect to phase separation have not been presented for all highly doped glasses mentioned before.

Recently, amplifying strip waveguides could be generated in  $\text{Ge}_{25}\text{Ga}_{10}\text{S}_{65}$  glasses doped with 15,000 ppm  $\text{Pr}^{3+}$  by a new photolithographic technique [3]. With a strip waveguide of a cross section of  $6\mu\text{m} \times 8\mu\text{m}$  and a length of 5.2 cm an internal gain of 0.3 dB at 1309 nm could be

detected for pumping at 1010 nm wavelength with intensities > 125 mW [3]. Calculations predict an internal gain of up to 6 dB at 400 mW pump intensity, assuming internal losses of 0.2 dB/cm in the waveguide. The discrepancy between the measured and the much higher calculated amplification was caused by high internal losses of 2.9 dB/cm in the strip waveguide due to scattering on crystalline phase separations and streaks. The microstructural characterization of the glasses showed GeS<sub>2</sub> crystallites with an average size of 10 to 50 μm in average distances of 50 - 200 μm [16]. The calculations [3] have also shown that a low intrinsic optical loss of the glass matrix is a very important for high gain, since a remarkable drop of the net gain is already obtained for losses ≥ 1 dB/cm.

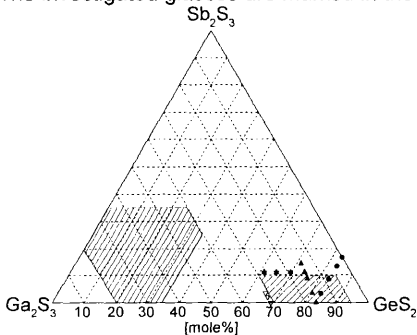
Therefore, the investigations of this paper were focused on the questions whether the crystallite formation in the 15,000 ppm Pr<sup>3+</sup> doped Ge<sub>25</sub>Ga<sub>10</sub>S<sub>65</sub> glasses could be suppressed by increasing the number of glass components and how monoliths with lengths of several centimeters could be fabricated from the modified glasses. In one series the Ge-Ga-S-glasses were modified with Sb. Sb was chosen, because it forms glasses with GeS<sub>2</sub> in a broad composition range [13] and is less poisonous than As. In a second series Ge<sub>25</sub>Ga<sub>10</sub>S<sub>65</sub> glasses were modified with Sn and I. However, these results will be published later [14].

### 3 EXPERIMENTAL

As precursors, Ge, Ga and Sb, with purities ≥ 99.999% and 99.9% Pr<sub>2</sub>S<sub>3</sub>, respectively, were employed. Sulfur of a purity of 99.999%, which was additionally purified, was received from Vitron Spezialwerkstoffe GmbH, Jena, Germany. 4 to 10 g batches were filled into fused silica ampoules in a glove box under nitrogen atmosphere. After vacuum sealing (10<sup>-4</sup> Pa) the ampoules were heated under rotation to a temperature of 950° C for 20 h and quenched in air. The Pr<sup>3+</sup> doping concentrations are referred in mol-ppm to the cations. The <sup>1</sup>G<sub>4</sub> level of Pr<sup>3+</sup> doped glasses was excited with a frequency trebled Nd:YAG-OPO laser at 1020 nm. <sup>1</sup>G<sub>4</sub>-<sup>3</sup>H<sub>5</sub> fluorescence decay and fluorescence emission spectra were measured with an InGaAs diode at room temperature. All lifetimes are quoted as effective lifetimes τ<sub>eff</sub>, which were calculated from the fluorescence decay curve according to the equation τ<sub>eff</sub> = 1/(t=0)<sup>-1</sup> ∫ I(t)\*dt (I: intensity of fluorescence decay) and allow a better comparison of low and high Pr<sup>3+</sup> doped samples, because at high Pr<sup>3+</sup> concentrations the fluorescence decay does not show a monoexponentiell behavior any more. Absorption measurements were conducted with a UV-VIS-NIR spectrometer Omega 20 (Bruins Instruments). The transformation (T<sub>g</sub>) and crystallization (T<sub>c</sub>) temperatures have been measured with differential thermal analysis (Seiko TG/DTA320) using a heating rate of 10 °K/min.

### 4 Results

The investigated glasses are marked in the ternary GeS<sub>2</sub>-Ga<sub>2</sub>S<sub>3</sub>-Sb<sub>2</sub>S<sub>3</sub>-diagram in fig. 1



**fig.1** : Investigated 15000 ppm Pr<sup>3+</sup> doped Ge-Ga-Sb-S-glass compositions in the ternary GeS<sub>2</sub>-Ga<sub>2</sub>S<sub>3</sub>-Sb<sub>2</sub>S<sub>3</sub>-diagram. The composition ranges claimed by Aitken and Newhouse [12] are depicted as shaded areas. Data for the glass compositions represented by the filled triangles and circles are given in table 1

Pr<sup>3+</sup> doped Ge-Ga-Sb-S glasses have also been investigated by Aitken and Newhouse [12]. But neither Pr<sup>3+</sup> fluorescence data nor optical properties of these glasses were reported. The composition ranges claimed by Aitken and Newhouse are depicted as shaded areas in fig. 1.

In one series (unfilled triangles in fig. 1) it was examined whether the homogeneity of the 15000 ppm Pr<sup>3+</sup> doped Ge<sub>25</sub>Ga<sub>10</sub>S<sub>65</sub>-glasses (corresponding 83,3GeS<sub>2</sub>-16,7Ga<sub>2</sub>S<sub>3</sub>) could be improved by an increased Ga-content in connection with an Sb<sub>2</sub>S<sub>3</sub>-modification. Starting from Ge<sub>19,1</sub>Ga<sub>17,1</sub>S<sub>63,8</sub>, Sb<sub>2</sub>S<sub>3</sub> was added, keeping the Ge-Ga-ratio constant. Using melting temperatures of 950 °C, all glasses were opaque and the homogeneity of the glasses was not improved by increasing the melting temperature to 1050 °C [16]. Therefore these glass compositions have not been investigated further.

In the next step, the glass formation was examined as a function of the Ga-Ge-ratio at a constant Sb<sub>2</sub>S<sub>3</sub>-content of 11 mole% (stars in fig. 1). These glasses were all transparent and red colored. However, microstructural characterization showed the formation of crystallites (assumed to be α-GeS<sub>2</sub> [15]) with diameters up to 12 μm in an average distance between 60 and 100 μm [16]. Consequently, these glass compositions are not suitable for the preparation of a planar waveguide. It might be possible that the homogeneity of these glass could be improved further by higher melting temperatures and/or faster cooling. However, these investigations have been rejected and the reason for the phase separation has not been investigated, with respect to other glass compositions leading to transparent monoliths.

The next series was started from the composition Ge<sub>25</sub>Ga<sub>10</sub>S<sub>65</sub> (corresponding 83,3GeS<sub>2</sub>-16,7Ga<sub>2</sub>S<sub>3</sub>), doped with 15000 ppm Pr<sup>3+</sup>. Here, Sb<sub>2</sub>S<sub>3</sub> was introduced as an additional glass forming compound of up to 14.3 mole%, keeping the Ge:Ga ratio constant. The compositions are shown in fig. 1 as filled triangles. The properties of 15000 ppm Pr<sup>3+</sup> doped Ge-Ga-Sb-S-glasses are listed in table 1 in comparison with the corresponding Ge<sub>25</sub>Ga<sub>10</sub>S<sub>65</sub>-glass.

**Table 1:** Batch composition\* (atom%), color, transformation temperature T<sub>g</sub>, crystallization temperature T<sub>c</sub>, effective fluorescence lifetime τ<sub>eff</sub>, peak position λ<sub>max</sub> and half bandwidth FWHM of the <sup>1</sup>G<sub>4-3</sub>H<sub>5</sub> fluorescence of Ge-Ga-Sb-S-glasses and a Ge<sub>25</sub>Ga<sub>10</sub>S<sub>65</sub>, all doped with 15000 ppm Pr<sup>3+</sup>

Composition	colour	T <sub>g</sub> [°C]	T <sub>c</sub> [°C]	τ <sub>eff</sub> [μs]	λ <sub>max</sub> [nm]	FWHM [nm]
Ge <sub>25</sub> Ga <sub>10</sub> S <sub>65</sub>	green	450	573	15 ± 2	1339 ± 1	63
Sb <sub>2</sub> S <sub>3</sub> -addition, filled triangles in fig. 1						
Ge <sub>23,8</sub> Ga <sub>9,5</sub> Sb <sub>2,0</sub> S <sub>64,8</sub>	brown	417	550	17 ± 2	1340 ± 1	63
Ge <sub>21,9</sub> Ga <sub>8,7</sub> Sb <sub>5,0</sub> S <sub>64,2</sub>	red	373	536	16 ± 2	1340 ± 1	63
Ge <sub>21,1</sub> Ga <sub>8,4</sub> Sb <sub>6,2</sub> S <sub>64,2</sub>	red	363	457	16 ± 2	1340 ± 1	63
Ge <sub>20</sub> Ga <sub>8</sub> Sb <sub>8</sub> S <sub>64</sub>	red	340	460	16 ± 2	1340 ± 1	62
Substitution of Ga by Sb, circles in fig. 1						
Ge <sub>25</sub> Ga <sub>8</sub> Sb <sub>2</sub> S <sub>64</sub>	brown	415	546	16 ± 2	1340 ± 1	63
Ge <sub>25</sub> Ga <sub>5</sub> Sb <sub>4</sub> S <sub>64</sub>	red	373	534	18 ± 2	1341 ± 1	61
Ge <sub>20</sub> Ga <sub>2</sub> Sb <sub>8</sub> S <sub>64</sub>	red-brown, opaque	352	466	120 ± 10	1341 ± 1	63
Ge <sub>20</sub> Sb <sub>10</sub> S <sub>64</sub>	brown, opaque	345	463	330 ± 30	1341 ± 1	76

\* it was shown by chemical analysis that the analysed glass compositions are in very good agreement with the batch compositions [16]

#### Sb<sub>2</sub>S<sub>3</sub>-addition at fixed Ge:Ga ratio (filled triangles in fig. 1)

Table 1 shows that the color of the Ge<sub>25</sub>Ga<sub>10</sub>S<sub>65</sub> glass changes from green to red by the incorporation of Sb, which may be attributed to the lower band gap of Sb<sub>2</sub>S<sub>3</sub> [16]. For annealing of the glasses, it is important to have a sufficiently high difference between the transformation

temperature and the crystallization temperature (working range  $T_c$ - $T_g$ ). Therefore, it was interesting to investigate the influence of Sb on these temperatures. Table 1 shows that the Sb modification leads to a drastic decrease of the transformation temperature which can be explained by its network modifying role (replacement of 4-valent Ge by 3-valent Sb). For glasses with low Sb concentrations of 2.0 and 5.0 atom% Sb, the crystallization temperature is decreasing not as strongly as the  $T_g$ , which leads to an increasing working range of up to 163 K for 5.0 atom% Sb. For higher Sb contents, a second crystallization peak is observed in the DSC measurements [16] which leads to a decreasing working range of 94 K (6.4 mole % Sb) and 120 K (8 atom% Sb). In literature, appropriate data was not available for comparison, however working ranges of about 100 K and more can be assumed to be suitable for annealing in practical application [15].

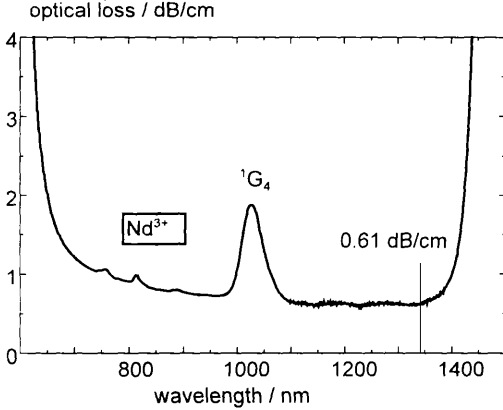
All glasses were free from crystalline phase separations [16] and exhibit the same fluorescence lifetimes and the same fluorescence maximum position and halfbandwidths as the unmodified  $\text{Ge}_{25}\text{Ga}_{10}\text{S}_{65}$ -glass within the error of measurement. The short fluorescence lifetimes can be attributed to concentration quenching effects but not to multiphonon relaxation effects as it has been shown by fluorescence lifetime measurements of appropriate Ge-Ga-S glasses with different  $\text{Pr}^{3+}$  concentrations and infrared spectroscopy [17], which showed that the glass matrix is transparent down to  $1100\text{ cm}^{-1}$  without remarkable (absorption coefficient  $< 0.5\text{ cm}^{-1}$ ) absorptions due to oxide, hydride, or OH impurities [17,18]. The short lifetimes do not exclude the realization of a planar amplifier with a net gain of several dB/cm, due to the high  $\text{Pr}^{3+}$  concentration [3].

#### Substitution of Ga by Sb (dots in fig. 1)

By substituting Ga subsequently by Sb, the glasses also darken with increasing Sb-content. The two glasses with low Sb contents of 2 and 4 atom% are transparent and free from crystalline phase separations [16]. Compositions with 8 and 10 atom% Sb were opaque and amorphous in X-ray diffraction analysis [16]. Therefore it has to be concluded that in these glasses 2 or more amorphous phases are present, which will have to be investigated more in detail in the future. The substitution of Ga versus Sb also leads to a decrease in the transformation temperature (see table 1), which can be attributed to the larger size of the  $^{51}\text{Sb}$  atom compared to  $^{31}\text{Ga}$ . In the case of clear glasses, the working range increases up to 161 K (4 atom% Sb), which is assumed to be sufficient for avoiding crystallization during annealing in practical application. For the opaque glasses, a working range of 114 K and 118 K was obtained.

The clear glasses exhibit the same fluorescence lifetimes as the unmodified Ge-Ga-S-glass (see fig.1 and discussion above). The  $\text{Pr}^{3+}$  fluorescence lifetimes of the opaque glasses have been determined to 120  $\mu\text{s}$  and 330  $\mu\text{s}$ , respectively. Unfortunately, quantitative NIR fluorescence measurements for the determination of the fluorescence intensities were not available. Therefore it can only be hypothesized that these long fluorescence lifetimes are caused by the existence of  $\text{Pr}^{3+}$ -rich and  $\text{Pr}^{3+}$ -depleted phases. Concentration quenching is less in the  $\text{Pr}^{3+}$ -depleted phases than in the  $\text{Pr}^{3+}$ -rich ones, which leads to longer fluorescence lifetimes. However, this would also lead to a decreased efficiency, because the  $\text{Pr}^{3+}$  ions in the  $\text{Pr}^{3+}$ -rich phase would not contribute to the long lifetime fluorescence. A similar effect has been reported by Almeida et al. [19], who investigated  $\text{Er}^{3+}$  sol gel derived oxide glass layers. The assumption of at least two different phases with  $\text{Pr}^{3+}$  is also supported by the fact, that for the Ga-free glass (see last line in table 1) with the longest fluorescence lifetime of about 330  $\mu\text{s}$ , the largest FWHM of about 76 nm (compared to about 63 nm for the other glasses) was determined. An increased half bandwidth of the  $\text{Pr}^{3+}$  fluorescence is indicating different chemical surroundings of the  $\text{Pr}^{3+}$  ions. A red shift of the fluorescence peak, which would indicate a less ionic character of the  $\text{Pr}^{3+}$  surrounding [20-22] caused by Sb, cannot be detected with sufficient significance.

In the next step, it was interesting to measure the intrinsic optical losses of the Sb doped glasses, because a low optical loss is required for high optical gain. For this purpose, the  $\text{Ge}_{20}\text{Ga}_8\text{Sb}_8\text{S}_{64}$  (e.g. the transparent glass with the highest amount of Sb, see table 1) was chosen, because it was definitely not included in the composition ranges of [12]. The result is shown in fig. 2.



**fig. 2:** Optical loss as function of wavelength for a 2.75 cm  $\text{Ge}_{20}\text{Ga}_8\text{Sb}_8\text{S}_{64}$  glass rod doped with 15,000 mole ppm  $\text{Pr}^{3+}$ , measured by vis-NIR spectroscopy

Fig. 2 shows the absorbance edge of the semiconductor transition at about 650 nm which can be assumed to be far away enough from the pump wavelength of the  $^1\text{G}_4$  level [20], which can be clearly seen in fig. 2 as a peak at about 1020 nm. The small peaks at 750 nm and 800 nm can be attributed to  $\text{Nd}^{3+}$  impurities in the  $\text{Pr}^{3+}$ -source [18]. For  $\lambda > 1400$  nm, the high  $^3\text{F}$  absorption band [20] can be detected. In the 1.3  $\mu\text{m}$  window, an optical loss of 0.61 dB/cm is obtained. The refractive index of this glass was measured to 2.24 at 1300 nm [16], which leads to a reflection loss of about 14.6 %, as it was calculated from Fresnel's equation [16]. After this correction, an intrinsic loss of only 0.05 dB/cm is obtained for the 1.3  $\mu\text{m}$  wavelength range. This is much

lower than the attenuation obtained in Sb free glasses of several dB/cm according to scattering losses [17].

So far, completely clear and stress free monoliths with lengths of up to 8 cm have been prepared on lab scale by melting at 1080 °C and annealing at  $T_g$  [16], which is assumed to be a good starting point for further optimization towards waveguide fabrication.

## 5 CONCLUSION

For the first time, highly transparent  $\text{Ge}_{25}\text{Ga}_{10}\text{Sb}_{65}$ -glasses doped with 15000 ppm  $\text{Pr}^{3+}$  have been obtained by modification with Sb. The high optical quality of these glasses leads to very low intrinsic optical losses, which is a decisive prerequisite for the future development of planar amplifiers with remarkable net gain. For this purpose, the codoping of the glasses with  $\text{Yb}^{3+}$  will have to be investigated in the future.

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