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Pr\textsuperscript{3+}-doped GeS\textsubscript{x}-based glasses for fiber amplifiers at 1.3 \(\mu\)m

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The photoluminescence properties of Pr\textsuperscript{3+}-doped GeS\textsubscript{x}-based glasses are studied and compared with those of other sulfide and fluoride glasses. The possibility of highly pump-power-efficient fiber amplifiers based on these GeS\textsubscript{x}-containing glasses in the telecommunications window at 1.3 \(\mu\)m is discussed.

Sulfide glasses doped with Pr\textsuperscript{3+} are among the most promising glasses for fiber amplifiers in the 1.3-\(\mu\)m optical telecommunications window, because these glasses have both a large stimulated-emission cross section of the \(1\text{G}_4 \rightarrow 3\text{H}_5\) gain transition and a high emission lifetime of the \(1\text{G}_4\) state.\textsuperscript{1,2} By means of a strong local electric field around Pr\textsuperscript{3+} the high refractive index of these glasses (\(n_2\)) induces a high radiative transition rate and hence a large cross section for the stimulated emission \(\sigma_e\). Alternatively, because of the low-phonon-energy character of these glasses the multiphonon relaxation rate of the nonradiative \(1\text{G}_4 \rightarrow 3\text{F}_4\) transition is low and results in an emission lifetime \(\tau_e\) higher than that observed in oxide and fluoride glasses. The product of \(\sigma_e\tau_e\) determines, along with fiber design parameters, the small-signal gain coefficient or pump power efficiency of a fiber amplifier.\textsuperscript{3} By use of ZBLAN (ZrF\textsubscript{4}±BaF\textsubscript{2}±LaF\textsubscript{3}±AlF\textsubscript{3}±NaF) fluoride glass, fiber amplifiers have already been developed,\textsuperscript{4,5} with 0.2 dB/mW as a typical pump power efficiency.

Here we report on the photoluminescence properties of Pr\textsuperscript{3+}-doped GeS\textsubscript{x} glasses and assess the attainability of highly efficient fiber amplifiers.

We melted various glasses in the GeS\textsubscript{x} and (GeS\textsubscript{x})\textsubscript{80}(Ga\textsubscript{2}S\textsubscript{3})\textsubscript{20} glass systems (\(x = 2, 3\)) by starting from 99.999% (5N) pure elements Ge and S and 6N pure Ga. The dopant Pr was added as 3N Pr\textsubscript{2}S\textsubscript{3}. These glasses were melted inside silica ampoules according to well-established procedures for chalcogenide glasses.\textsuperscript{6} The various starting materials were stored, weighed, and batched into the ampoules in a glovebox under an Ar atmosphere. The ampoules were sealed off with a natural gas±oxygen flame under a vacuum of \(10^{-3}\) to \(10^{-4}\) mbar. During melting at 1000 \(^\circ\)C the ampoules were rotated. We homogenized the melts, and after quenching we annealed the glasses. By mixing the appropriate fluorides we melted ZBLAN fluoride glasses under a reactive atmosphere of Ar±SF\textsubscript{6} in glassy C crucibles.\textsuperscript{7}

Pr was excited directly into the \(1\text{G}_4\) state by a Ti:sapphire laser near 1 \(\mu\)m. The \(1\text{G}_4 \rightarrow 3\text{H}_5\) photoluminescence from the glass samples was focused on the entrance slit of a monochromator, and its intensity was measured by a Ge photodetector cooled with liquid N\textsubscript{2} by use of lock-in techniques to improve the signal-to-noise ratio. A cryostat permitted us to measure in the temperature range of 10 to 300 K. In Fig. 1 the normalized room-temperature photoluminescence spectra of Pr\textsuperscript{3+}-doped ZBLAN, GeS\textsubscript{2}, and (GeS\textsubscript{x})\textsubscript{80}(Ga\textsubscript{2}S\textsubscript{3})\textsubscript{20} are shown. The covalent character of the sulfide glasses results in a spectral shift of the peak luminescence from 1.32 \(\mu\)m in ZBLAN to 1.34 \(\mu\)m in GeS\textsubscript{2}. The full width at half-maximum of the photoluminescence in GeS\textsubscript{2} glass is 110 nm, considerably larger than the 80 nm in (GeS\textsubscript{x})\textsubscript{80}(Ga\textsubscript{2}S\textsubscript{3})\textsubscript{20} and the 90 nm in ZBLAN.

Multiphonon relaxation in Pr\textsuperscript{3+}-doped GeS\textsubscript{2} glass is determined predominantly by the number of phonons required for bridging the energy gap between the \(1\text{G}_4\)
The quenching mechanism in Pr-doped GeS$_2$ glass is mainly due to the Boltzmann constant. If the only luminescence quenching mechanism in GeS$_3$ glass and which are absent in GeS$_2$, then the emission lifetime $t$ is given by

$$t = \frac{\tau_e}{[1 + W_{mr}(T)\tau_r]},$$

where $p$ is the number of phonons that bridge the energy gap and $\hbar \omega$ is the phonon energy. Only phonons of a single energy are assumed to be active in the nonradiative transition. $W_{mr}(0)$ is the multiphonon relaxation rate near 0 K, and $k$ is the Boltzmann constant. The multiphonon relaxation rate $W_{mr}$, as a function of temperature $T$, is

$$W_{mr}(T) = W_{mr}(0)[(\exp(h\omega/kT) - 1)^{-1} + 1]^p,$$

where $p$ is the number of phonons that bridge the energy gap requires and $\hbar \omega$ is the phonon energy. Only phonons of a single energy are assumed to be active in the nonradiative transition. $W_{mr}(0)$ is the multiphonon relaxation rate near 0 K, and $k$ is the Boltzmann constant. The multiphonon relaxation rate $W_{mr}$, as a function of temperature $T$, is

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$$W_{mr}(T) = W_{mr}(0)[(\exp(h\omega/kT) - 1)^{-1} + 1]^p.$$
Table 3. Radiative Properties of Pr$^{3+}$ in Fluoride and Sulfide Glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\tau_e$ (µs)</th>
<th>$\tau_d$ (µs)</th>
<th>$\beta^a$</th>
<th>$\eta$ (%)</th>
<th>$(\sigma_e - \sigma_{\text{ESA}})\tau_e$ ($\times 10^{-26}$ cm$^2$s)$^b$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZBLAN</td>
<td>110$^c$</td>
<td>2484</td>
<td>0.60</td>
<td>4</td>
<td>36</td>
<td>This study</td>
</tr>
<tr>
<td>(Ge$<em>{S_2}$)$</em>{80}$(Ga$_2$S$<em>3$)$</em>{20}$</td>
<td>320</td>
<td>540</td>
<td>0.50</td>
<td>59</td>
<td>250</td>
<td>This study</td>
</tr>
<tr>
<td>Ga–La–S</td>
<td>295/300</td>
<td>500/510</td>
<td>0.52</td>
<td>58/60</td>
<td>250</td>
<td>1, 2</td>
</tr>
<tr>
<td>Ge$_{S_2}$ (x = 2, 2.5, 3)</td>
<td>360</td>
<td>—</td>
<td>—</td>
<td>90</td>
<td>—</td>
<td>This study</td>
</tr>
<tr>
<td>(Ge$<em>{S_2}$)$</em>{80}$(Ga$_2$S$<em>3$)$</em>{20}$</td>
<td>320</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>This study</td>
</tr>
<tr>
<td>Ge–As–S</td>
<td>337</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>16</td>
<td>This study</td>
</tr>
<tr>
<td>As–S</td>
<td>250</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>17</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $\beta$ is the branching ratio of the $^1G_4\rightarrow^3H_5$ transition.

$^b$ Values for $(\sigma_e - \sigma_{\text{ESA}})\tau_e$ were obtained at the wavelength of 1.31 µm.

$^c$ Ref. 4.

...The accuracy of the Judd–Ofelt analysis for (Ge$_{S_2}$)$_{80}$(Ga$_2$S$_3$)$_{20}$ glass is limited because the ground-state absorptions to the $^3P_0$ and $^3P_1$ states are obscured by the glass absorption edge, and their oscillator strengths cannot be included in the analysis.

The Judd–Ofelt parameters were used to determine the radiative lifetime of the Pr$^{3+}$ $^1G_4$ state. In combination with photoluminescence spectra of the $^1G_4\rightarrow^3H_5$ and $^1D_2\rightarrow^3G_4$ transitions (we populated the $^3D_2$ state by pumping with an Ar-ion laser) it was also possible to calculate the cross sections for stimulated emission and for the gain-limiting process of excited-state absorption (ESA) (of signal photons in the $^1G_4\rightarrow^1D_2$ transition). The procedure for obtaining both cross sections was described previously for ZBLAN, and our results for this glass are in good agreement. The cross sections $\sigma_e$ and $\sigma_{\text{ESA}}$ as well as the shape of the gain curve, given by $\sigma_e - \sigma_{\text{ESA}}$, are presented for (Ge$_{S_2}$)$_{80}$(Ga$_2$S$_3$)$_{20}$ glass in Fig. 3. In Table 3 the $(\sigma_e - \sigma_{\text{ESA}})\tau_e$ product (which determines the pump power efficiency of a fiber amplifier) and other radiative parameters for various sulfide glasses and ZBLAN are listed.

The $(\sigma_e - \sigma_{\text{ESA}})\tau_e$ product of (Ge$_{S_2}$)$_{80}$(Ga$_2$S$_3$)$_{20}$ chalcogenide glass is $250 \times 10^{-26}$ cm$^2$s, comparable with that of Ga–La sulfide glass$^4$ and nearly seven times that of ZBLAN. This would provide for high pump power efficiencies of the order of 1 dB/mW with adequate fiber design parameters. However, the fiber draw regime has yet to be determined for Ge–Ga sulfide glass.

The fiber draw regime for Ge$_{S_2}$ glasses starts near $x = 2$. The drawback of Pr-doped Ge$_{S_2}$ fibers, although their emission lifetime is as high as 360 µs, would be the low dopant level, and this would require relatively long lengths of doped fiber with low intrinsic background absorption losses.

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A. J. Faber is also with the Institute of Applied Physics TNO, 5600 AN Eindhoven, The Netherlands.

References

14. See, for example, R. S. Quimby and W. J. Miniscalco, J. Appl. Phys. 75, 613 (1994).