Sulphide glasses for optical amplifiers

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Abstract. Sulphide glasses are good host materials for rare earth ions and then can be considered for optical amplification in telecommunication transmissions. Indeed, for WDM (Wavelength Division Multiplexing) applications, amplifiers from 1, 2 to 1, 7µm are needed. Silicate, telluride and fluoride are interesting hosts but limited by their phonon energies. In contrast, sulphide glasses exhibit phonon energy lower than well-used oxide or fluoride glasses and then new radiative transitions are available. In particular, dysprosium ions can emit a signal around 1.3µm as well as praseodymium, while thulium and erbium improve the absorption and emission cross sections compare to oxides, shifting the spectral band however. Nevertheless, there is still some drawbacks to overcome before using this material as a commercial optical amplifier. Firstly, fibres with losses around 1dB/m are necessary. Then, multiphonon relaxation mechanisms are not very well understood and there is still some problems to establish the empirical “energy-gap law”. Host absorption, large refractive index, different sites, impurities may also have to be considered.

Key words: Rare earth, amplifier, sulphide glasses, multiphonon relaxation

Introduction

Silica fibers are mainly used in telecommunications; their losses are lower than 0.4dB/km in the range of 1.2 to 1.6µm. Even if these losses are low, a signal traveling in these fibers need to be amplified by a gain between 20 and 30dB each around 100km. Solutions based on rare earth doped fiber amplifier are mainly studied. Currently, Erbium Doped Fiber Amplifiers (EDFA) are used [1] around 1.5µm on the so-called C and L band usually based on silica matrix. Praseodymium Doped Fiber Amplifier (PDFA) modules are also commercially available [2] since 1991 for the amplification around 1.3µm on fluoride matrix. The more recent amplifier based on rare earth ions is the TDFA, Thulium Doped Fiber Amplifier, an efficiency higher than 50% has been achieved using different configurations [3, 4].
Due to their low phonon energy chalcogenide glasses are promising host for amplifiers. Mainly two different families of sulfide have been studied GeGaS and GaLaS. First studies have been done for the second telecommunication window around 1.3\(\mu\)m. Performances of dysprosium [5] and praseodymium [6] have been evaluated for amplification applications in sulfide glasses. In this last reference, the better efficiency for 1.3\(\mu\)m amplification has been achieved (0.81dB/mW at 1.34\(\mu\)m) in a single mode fiber with 1.2dB/m losses at 1.31\(\mu\)m. Even if these losses are quite high it can be interesting to evaluate the possibility of using thulium for amplification in sulfide glasses. These glasses offer low non radiative probability (low phonon energy), high radiative rate (high index of refraction so high local field correction) and shifted band to the infra-red (high covalency) [7].

To characterize gain of an amplifier there is three main values, the absorption and emission cross sections and the quantum efficiency, the part of radiative probability in a transition. So, an important data to know is the non radiative rate (W_{NR}) of the transitions. It has been shown that this parameter can be described by a multiphonon process depending on the energy gap and the highest phonon energy in the matrix. A complete study in different oxide glasses is presented in [8]. For the sulfide glasses, the parameters for multiphonon rates are usually taken in reference [9], where R. Reisfeld presents a review of radiative and non radiative properties of rare earth in amorphous media. Nevertheless, the law presented in this paper for sulfide materials seems anomalous compared to other glasses. We will discuss here as Quimby [10] the adequacy to take new parameters for the energy gap law describing the multiphonon relaxation in our sulfide glasses.

In this paper, we will present, in a first part, the sulfide glass we have studied and their main optical characteristics. In a second part, the measured cross sections and decays will be reported and the energy gap law deduced from low temperature measurements will be analysed. Finally, the advantages and disadvantages of sulfide glasses to realize an amplifier will be discussed.

The host

The sulfide glass we have studied is a germanium gallium sulfide glass stabilized with antimony, Ge_{20}Ga_{5}Sb_{10}S_{65} usually referred as 2G2S, its fabrication is presented in [11].

This glass presents a weak crystallization peak and a high thermal stability, it’s then a good candidate to draw fiber.

This glass is also transparent from 0.6 to 11\(\mu\)m, its maximum transmission is 65% and its color is red.

A chemical purification is done to eliminate impurities but there is still some vibrations due for example to the presence of hydrogen near 4\(\mu\)m (S-H bonds).

The Raman spectrum presents a main peak around 340cm\(^{-1}\) due to Ge-S vibrations and a weak band in the region of 600-800cm\(^{-1}\) may be due to residual oxygen presence in the material.

As detailed in [12], refractive index has been measured using a prism coupling method from 0.55 to 1.55\(\mu\)m as shown in Figure 1. We can see on this figure that the index of refraction of GeGaSbS is high, 2.25 at 1.55\(\mu\)m.

Finally, the solubility of rare earth in this glass is not too bad, it is possible to incorporate up to 1at% of rare earth in this host.
Rare earth measurements

The first parameters we have to determine to realize an amplifier are the absorption and emission cross sections and the lifetimes of the different levels involved in the laser transition.

Absorption cross section is easy to determine if it’s possible to make a bulk sample. It is necessary to measure the absorption coefficient $\alpha(\lambda)$ and determine the number $N$ of ions per unit of volume (ions/cm$^3$):

$$\sigma(\lambda) = \frac{\alpha(\lambda)}{N}$$  \hspace{1cm} (Eq. 1)

As an example, absorption cross section of thulium ions in 2G2S compared to a well known fluoride glass (ZBLAN) is reported in Figure 2. We can see that the matrix absorption of the sulfide glass started near 650nm but in the infrared the peak cross section is about five times higher in sulfide glass compared to fluoride.

For the quantum efficiency, it is important to know the measured lifetime ($\tau_{mes}$) at room temperature and the radiative lifetime ($\tau_{rad}$) of a level. The measured lifetime and the radiative one represent respectively the total and the radiative emission rates of a level ($W_{tot}$, $W_{rad}$). Theoretically, at low concentration and low pump power, there is no transfer and up-conversion, so, it is possible to assume that the non radiative part ($W_{nrad}$) of the emission is only due to multiphonon relaxation ($W_{mp}$):

$$\frac{1}{\tau_{mes}} = W_{tot} = W_{rad} + W_{nrad} = W_{rad} + W_{mp}$$  \hspace{1cm} (Eq. 2)

It is well known that on bulk sample there is another phenomenon that can affect the measured lifetime ($\tau_{mes}$), the so-called re-absorption. A photon emitted by an ion can be re-absorbed by another ion, this radiative energy transfer increases the observed lifetime. Experimentally, this phenomenon can be reduced when sample is geometrically small on a fine plate or on a powder form, for instance. Moreover, it is not always sufficient to use powder to avoid internal reflection and more sophisticated detection techniques have been
proposed to decrease the radiation trapping [13]. In our experiments the samples were on a powder form.

![Figure 2: Absorption cross section of thulium ions in 2G2S compared to ZBLAN glass](image)

There are different methods to determine radiative lifetime. Classically, the Judd-Ofelt analysis is used to calculate the radiative probability of the excited state of the rare earth ions [14, 15, 16]. It is commonly assumed that to achieve this calculation, 5 or 6 absorption bands are necessary. As we can see in Figure 2, there are only 4 visible bands for Tm3+ due to host absorption. We are then in poor condition for sulfide glass to applied this approach.

A more direct possibility to determine the radiative probability \(A_{\text{rad}}\) is to integrate the individual absorption bands from a multiplet \(J\) to a multiplet \(J'\) knowing the refractive index \(n\) and using the following expression derived from the second Einstein relation (Fuchtbauer-Ladenburg, FL) [17]:

\[
A_{\text{rad}} = \frac{1}{\tau_{\text{rad}}} = 8\pi cn^2 \frac{2J + 1}{2J' + 1} \int \sigma_a(\lambda) d\lambda 
\]

(Eq. 3)

Finally, it is also possible to measure the radiative lifetime if the non radiative relaxation is negligible. This can be the case at very low temperature when the energy gap between two adjacent levels is high enough. We have reported in Table 1 the values obtained for the radiative lifetimes of different levels of erbium and thulium ions using the techniques described above. We can see that the measured lifetime is always higher than the calculated one. We know if there is some radiation trapping (re-absorption) the lifetime will appear higher but we have taken care (low concentration, powder) to measure this lifetime. Then we argue the hypothesis as [18] that a local index of refraction can exist around the rare earth different from the bulk refractive index. This local refractive index may be due to change of covalency for the Ln-S bond or other effects due to impurities as oxides near the rare earth ions. The recalculated index of refraction is presented in Figure 3.
Table 1: Radiative lifetime obtained by different methods, Judd-Ofelt (JO), Ladenburg- Fuchtbauer (LF) and measured at 10K for different levels of rare earth ions.

<table>
<thead>
<tr>
<th></th>
<th>Er 4I_{11/2}</th>
<th>Er 4I_{13/2}</th>
<th>Tm 3H_{4}</th>
<th>Tm 3H_{5}</th>
<th>Tm 3F_{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>JO</td>
<td>1.55</td>
<td>1.85</td>
<td>0.12</td>
<td>0.65</td>
<td>0.85</td>
</tr>
<tr>
<td>LF</td>
<td>1.70</td>
<td>1.86</td>
<td>0.13</td>
<td>0.83</td>
<td>0.84</td>
</tr>
<tr>
<td>10K</td>
<td>1.60</td>
<td>2.90</td>
<td>0.15</td>
<td>0.85</td>
<td>1.30</td>
</tr>
</tbody>
</table>

Knowing the measured ($\tau_{mes}$) and radiative lifetime ($\tau_{rad}$) it is possible to determine the energy gap law [8]. At a given temperature $T$, it is first necessary to determine the rate of multiphonon relaxation ($W_{mp}$) for different levels:

$$W_{mp}(T) = \frac{1}{\tau_{mes}(T)} - \sum \frac{1}{\tau_{rad}(T)}$$

Then it is possible to plot the variation of $W_{mp}(T)$ with the energy gap $\Delta E$ and finally adjusted, at low temperature, this curve with the empirical law:

$$W_{mp}(T) = C \exp[-\alpha\Delta E]$$

As an example, we have reported in Figure 4 the variation of the multiphonon rate with the energy gap the so called “energy gap law”, at 80K.

One can see that there are two different curves depending on the energy gap, the first one when the gap is higher than 2500cm$^{-1}$ ($C=1.1 \times 10^{6}$ s$^{-1}$ and $\alpha=1.8 \times 10^{-3}$cm), the second one when the gap is lower ($C=3.7 \times 10^{9}$ s$^{-1}$ and $\alpha=6.9 \times 10^{-3}$cm). A drastic difference is observed between the C parameters especially. The first set of parameters can be compared with the ones obtained by Reisfeld [9] and the second one with the others obtained by Quimby [10]. In this last paper it is assumed that there is another non-radiative process affecting the total non-radiative rate as residual rare earth clustering, energy transfer to the host, impurities. We conclude that, for energy gap lower than 2500cm$^{-1}$, it is not possible to use the classical law obtained in [9].
Finally, the last parameter we have to determine is the emission cross section. There are two common ways to do it, using the Fuchtbauer-Ladenburg (FL) method or the Mac Cumber (MC) one. In the first method, the index of refraction and the radiative lifetime are needed, branching ratio is also necessary if there is more than one transition from the emitted level. In the second method, the absorption and the position of the Stark levels are needed. The difficulty comes from determination of this last parameter, Miniscalco and Quimby [19] have proposed a simplified technique for erbium in glasses. We can see in Figure 5 and Figure 6 the absorption and emission cross sections for the $^{3}H_{5}$-$^{3}H_{6}$ transition in 2G2S : Tm3+. Emission cross section has been determined by the two techniques cited above. A large discrepancy is observed between them when the measured index of refraction (Figure 5) is used; in contrary a good agreement is obtained with the re-calculated index (Figure 6).

**Figure 4**: Energy gap law at 80K.

**Figure 5**: Absorption (SEA) and Emission cross sections (FL, Fuchtbauer-Ladenburg and MC, Mac Cumber) for the $^{3}H_{5}$-$^{3}H_{6}$ transition in 2G2S : Tm3+ using the measured index of refraction.
Conclusion

We have shown how to determine the main spectroscopic parameters (absorption and emission cross section and quantum efficiency) to quantify the gain of an amplifier. To explain our measurements we have proposed the assumption of a local refractive index around the rare earth ions different from the one of the host. This assumption could be based on presence of impurities as oxides in the samples. Nevertheless, we know that experimental determinations can be affected by re-absorption process and further measurements are needed to confirm our hypothesis. An energy gap law has been determined for our sulphide glass and we found two different laws depending on the value of the energy gap (> or < 2500cm⁻¹). This may be also due to the impurities. New purification seems necessary. Nevertheless, we can conclude that it is possible to realize optical amplification in sulphide glass with a careful determination of spectroscopic parameters. Because of the high index of refraction and then induced nonlinear effects rare earth doped sulfide glasses are promising host for self doubling frequency or to achieve other higher order resonant optical non linear effects.

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